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## A Molecular Beam Mass Spectrometric Study of the Formation and Photolysis of ClO Dimer

Final Report

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For NASA Headquarters

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## **A Molecular Beam Mass Spectrometric Study of the Formation and Photolysis of ClO Dimer**

**Final Report**

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**MRI Project No. 9316/17/18-A**

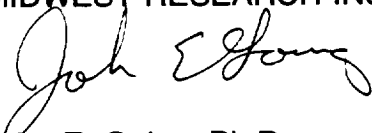
**March 6, 1992**

## PREFACE

This final report covers research performed on NASA Contract No. NASW-4371. Dr. Frank T. Greene and Dr. David Robaugh served as coprincipal investigators. Mr. Gil Radolovich, Head, Mass Spectrometry Section, had administrative responsibility for this work. The NASA technical officer was Dr. Michael Kurylo.

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March 6, 1992

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## ABSTRACT

An investigation of the chlorine oxides present at temperatures and pressures typical of the Antarctic stratosphere was carried out. A series of low temperature flow reactors was constructed and used in conjunction with molecular beam mass spectrometric techniques to identify species and characterize their kinetic behavior at temperatures of  $-20$  to  $-70^{\circ}\text{C}$  and pressures of from 30 to 130 Torr.

It was found that the gas phase chlorine-oxygen system was quite complex at low temperatures; characterization of these systems was required before the major tasks could be undertaken. ClO dimer was unambiguously identified and found to be thermodynamically very stable under stratospheric conditions. It was also found that any system which contained  $\text{ClO}_2$  and ClO also contained a larger oxide. This oxide was identified by mass spectrometric and velocity analysis techniques as  $\text{Cl}_2\text{O}_3$ . A survey of possible higher oxides, which have been postulated as possible chlorine sinks in the stratosphere, was also carried out. Only low concentrations of chlorine-oxygen species having molecular weights between those of  $\text{Cl}_2\text{O}_3$  and  $\text{Cl}_2\text{O}_8$  were detected in several chemical systems.

The rate of formation of ClO dimer was measured as a function of temperature and pressure. Measurements were made of both the decay of ClO and the formation of the dimer. By comparing these rates it was determined that virtually all of the ClO was converted to the dimer under stratospheric conditions, and that the other ClO reactions were not important under these conditions. The rate constants for formation of the dimer from ClO were measured at temperatures from  $-20^{\circ}$  to  $-70^{\circ}\text{C}$  and pressures from 30 to 120 Torr.

The experimental problems in determining the reaction products produced by the photolysis of the dimer were analyzed, a suitable experiment devised, and the apparatus assembled. The initial experiments have not yet been carried out.

## SECTION 1

### INTRODUCTION

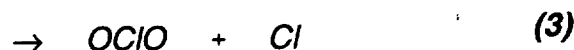
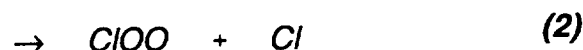
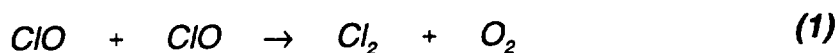
The dimer of ClO has been proposed as a key intermediate in the catalytic destruction of ozone in the Antarctic stratosphere. To date, evidence for the existence of this transient molecule has come from infrared and ultraviolet spectroscopic observations in laboratory studies. This investigation was undertaken principally to obtain a definitive mass spectrometric identification of the dimer and to determine its rate of formation and photochemical behavior. These measurements were to be made using molecular beam mass spectrometry (MBMS) in conjunction with a flow reactor(s) and ancillary techniques including optical spectroscopy and laser techniques.

The chlorine-oxygen system, under conditions typical of those found in the Antarctic stratosphere, was found to be much more complex than had been reported at the time the proposal was formulated. Consequently, it was necessary both to evaluate a number of chemical systems and to make a preliminary characterization of the species present before the planned experiments could be undertaken. The results obtained include an unambiguous identification of the dimer, the determination of the rate of formation of the dimer at stratospheric temperatures and pressures, preliminary identification and characterization of the adduct  $\text{ClO} \cdot \text{ClO}_2$ , and a survey of higher chlorine oxides present under stratospheric conditions.

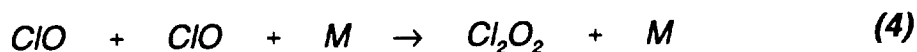
## SECTION 2

### BACKGROUND

The self-reaction of ClO radicals has been the subject of several investigations employing a variety of techniques including flash photolysis, discharge flow, modulated photolysis, and flash-photolysis kinetic spectroscopy.<sup>1,2</sup> From the combined results of these studies it is generally agreed that at low pressures this reaction is second order in ClO and proceeds via three pressure independent bimolecular channels as follows:



However, there is considerable uncertainty in the relative importance of the three channels. Evidence of a fourth reaction channel



for the removal of ClO was first obtained by Johnston et al.<sup>3</sup> through studies of the photolysis of Cl<sub>2</sub>/O<sub>2</sub> mixtures by modulated photolysis techniques. Their measured overall rate was found to be linearly dependent on pressure over the range of 50 to 100 torr. In later work Cox et al.,<sup>4</sup> and Basco and Hunt<sup>5</sup> confirmed the pressure dependence and observed absorptions in the UV which they attributed to the dimer. Both groups proposed that the dimer formation at moderate pressures was either the dominate reaction or the rate limiting step in the removal of ClO under their experimental conditions. Hunt and Basco also obtained evidence that, in the presence of molecules such as Cl<sub>2</sub>O or ClO<sub>2</sub> which

are effective radical scavengers, ClO radicals reach an equilibrium with the dimer and calculated an equilibrium constant of  $3.1 \times 10^6$  L/mole at 298K. They also estimated that the dimer was very stable in this environment with a half-life of from 0.2 to 0.4 s. Further evidence for the formation of the dimer was obtained in the FTIR studies of Molina and Molina,<sup>6</sup> who attributed bands observed in a flow system where ClO was produced from ClO<sub>2</sub> to two forms of the dimer: ClOOCl and ClOClO.

Later UV and IR studies by Burkholder, et al.,<sup>7</sup> and Cox and Hayman<sup>8</sup> produced spectra which differed from those obtained by Molina and Molina and concluded that the reported spectrum of Molina and Molina was not due to dimer but to the adduct Cl<sub>2</sub>O<sub>3</sub>. Burkholder, et al., also reported that the ClO<sub>2</sub> system was complex and found that the absorption assigned to the adduct decreased on addition of ClO<sub>2</sub> and suggested that additional higher oxides were being formed. Later Parr, et al.,<sup>9</sup> reported measurements of the rate of formation of the adduct and higher chlorine oxides may be important reservoirs of active chlorine under the conditions of the Antarctic stratosphere.

From microwave spectra Birk, et al.,<sup>10</sup> have identified the symmetric ClOOCl isomer to be the major product of the ClO self reaction. Later DeMore and Tschuikow-Roux<sup>11</sup> reported a UV cross section for the dimer and also concluded that ClOOCl is the only isomeric form of the dimer produced in these systems.

There has been a mass spectrometric observation of the dimer reported by Friedl and Sanders<sup>12</sup> in studies of the reaction of ClO + BrO. They measured signals at  $m/e = 102$ , 104, and 106 which exhibited the correct isotopic ratio. They made no further efforts to identify these signals as being due to the dimer.

Both the equilibrium constant<sup>8</sup> and the rate of formation<sup>13</sup> of the dimer have been measured as a function of temperature. Unfortunately many studies have not been performed at the low temperatures or pressures of interest to the Antarctic ozone problem. In addition, there are discrepancies in the reported rate constants for the self reaction of ClO at low temperatures<sup>13</sup>, and no direct real time measurements of dimer formation.

Virtually all of the studies of the ClO dimer to date have been done by optical spectrometry, generally by UV absorption where transient bands have been observed and attributed to the dimer. The principal other evidence comes from the observed pressure dependence of the overall rate of disappearance of ClO. Considering the potential importance of the ClO dimer in atmospheric chemistry, a positive identification and more data on its kinetic and photochemical behavior were needed.



## **SECTION 3**

### **EXPERIMENTAL**

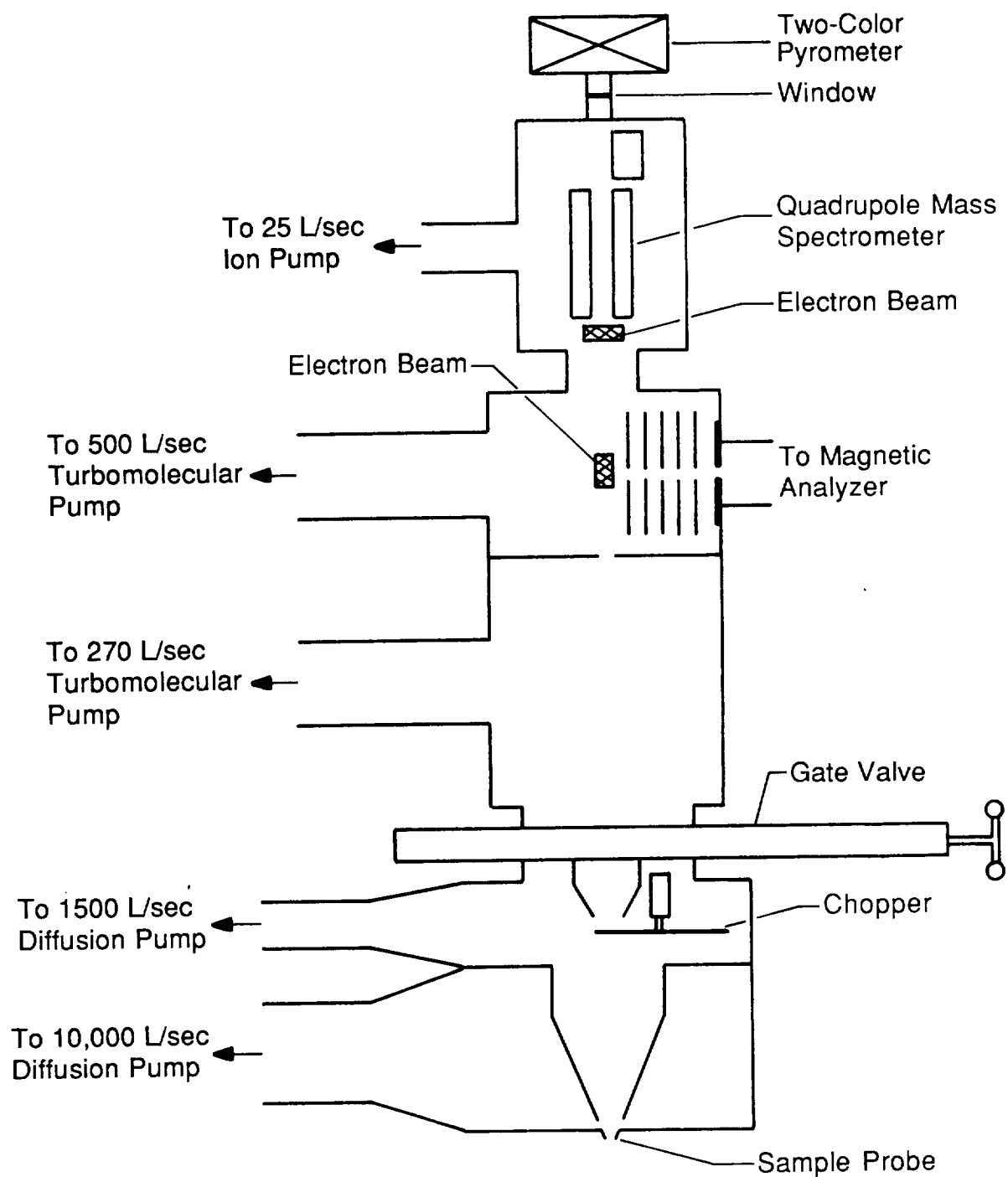
This research required the construction of a variety of flow reactors which have been used in conjunction with molecular beam mass spectrometry (MBMS), and various light sources and other ancillary equipment. The MBMS system, the flow reactors, and the ancillary equipment are discussed in the following sections.

#### **THE MOLECULAR BEAM MASS SPECTROMETRIC (MBMS) SYSTEM**

Molecular beam mass spectrometry was the principal technique used on this project for the identification and measurement of gaseous species. In this technique the gas being sampled is drawn through a small orifice in the sampling probe and expanded to essentially collisionless flow. At moderate to high pressures the expansion will be as a free-jet. This free-jet is then collimated into a molecular beam which is introduced into the ion source of the mass spectrometer. Because the free-jet expansion produces an extremely rapid drop in temperature and pressure, thereby quenching the sampled species, and because the sampled gas does not contact any surfaces during sampling and mass spectrometric analysis, high pressure MBMS can be used to study unstable species ranging from free radicals to high temperature oxides. Because the beam formation process is highly reproducible, this technique is capable of high analytical precision. The technique is also quite sensitive. With the MRI equipment, concentrations at part-per-billion levels have been measured.

The MBMS system used for these studies, shown in Figure 1, is a single-focusing magnetic mass spectrometer with a 12-in radius, which has a demonstrated resolution, based on the 10% valley criterion, in excess of 5,000. This instrument is being modified by the addition of an electrostatic sector, which will increase the resolution to 30,000. It is equipped with a nonmagnetic ion source with a well-collimated electron beam which has been shown to have a minimum energy spread for appearance potential and low ionizing energy measurements.

The data acquisition equipment used with the MBMS systems provides for phase-sensitive detection, ion counting, signal averaging, and time-of-flight velocity analysis. In addition, a Teknivent Vector 1 and a Finnegan Incos data



NOT TO SCALE

**Figure 1. Schematic of the molecular beam sampling system used with the high resolution magnetic and quadrupole spectrometers.**

system are available to control and acquire data from either the quadrupole or the magnetic sector mass spectrometers.

## **FLOW REACTORS**

Several flow reactors were constructed to meet the requirements of various experiments. These flow reactors, which heavily utilized existing components, were constructed to be readily interchangeable in order to facilitate switching between different experiments. The two basic flow reactor configurations are discussed in the following subsections.

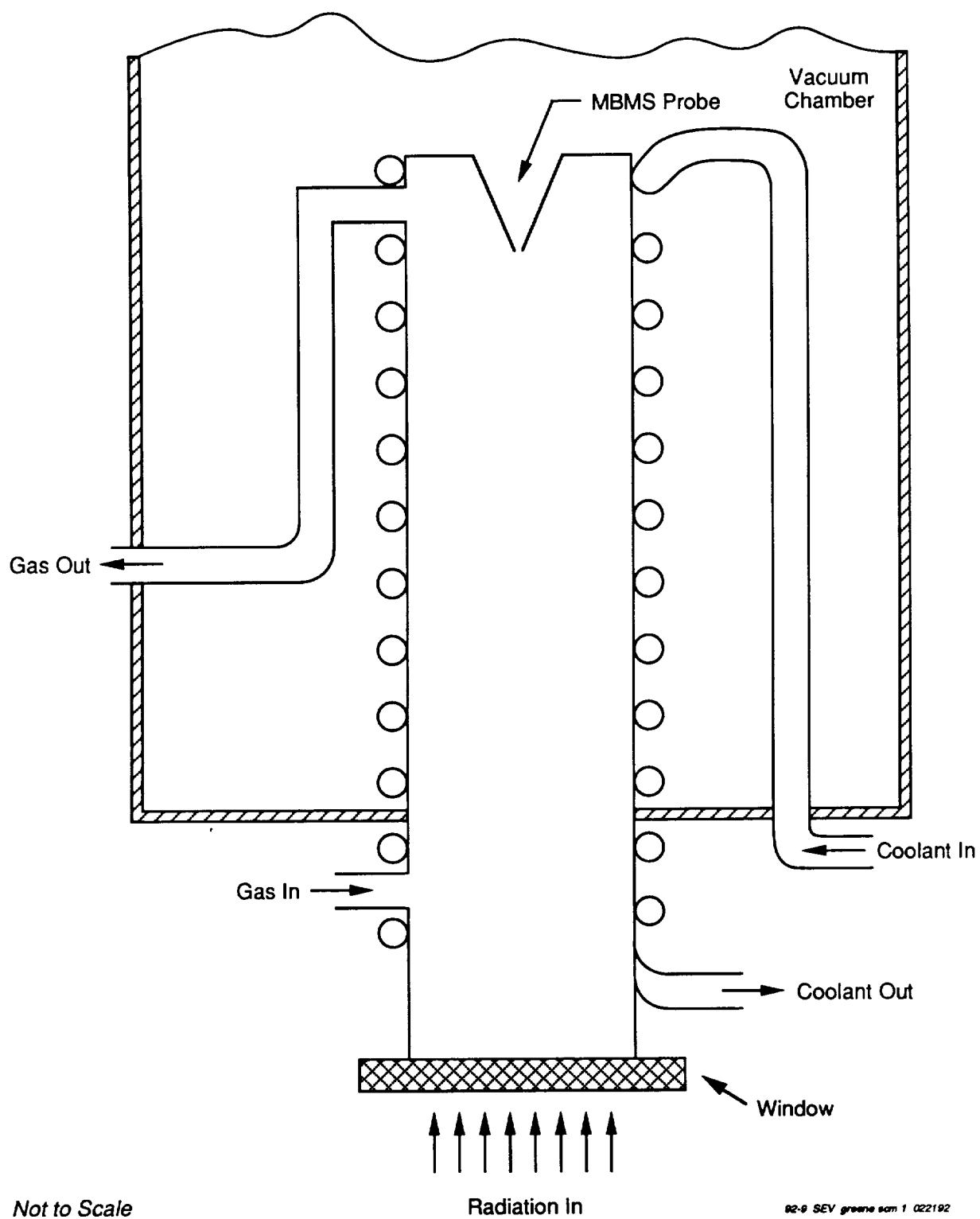
### **The Photochemical Flow Reactor**

The photochemical flow reactor, which was used principally for the initial survey and identification experiments, is shown schematically in Figure 2. This reactor consists of a vertical flow tube which contains a MBMS probe at the upper end and a window assembly at the lower end. The temperature of the upper portion of the flow tube and the MBMS probe assembly, which are coated with halocarbon wax,<sup>14</sup> is controlled by the circulation of methanol through tubing brazed to the outside surfaces. The cooled surfaces are vacuum jacketed. Reactant gases are introduced into the lower, room temperature end of the reactor and are irradiated continuously by 300 to 400 nm radiation from a filtered 1000 W Hg-Xe lamp and are cooled while flowing upward toward the MBMS probe.

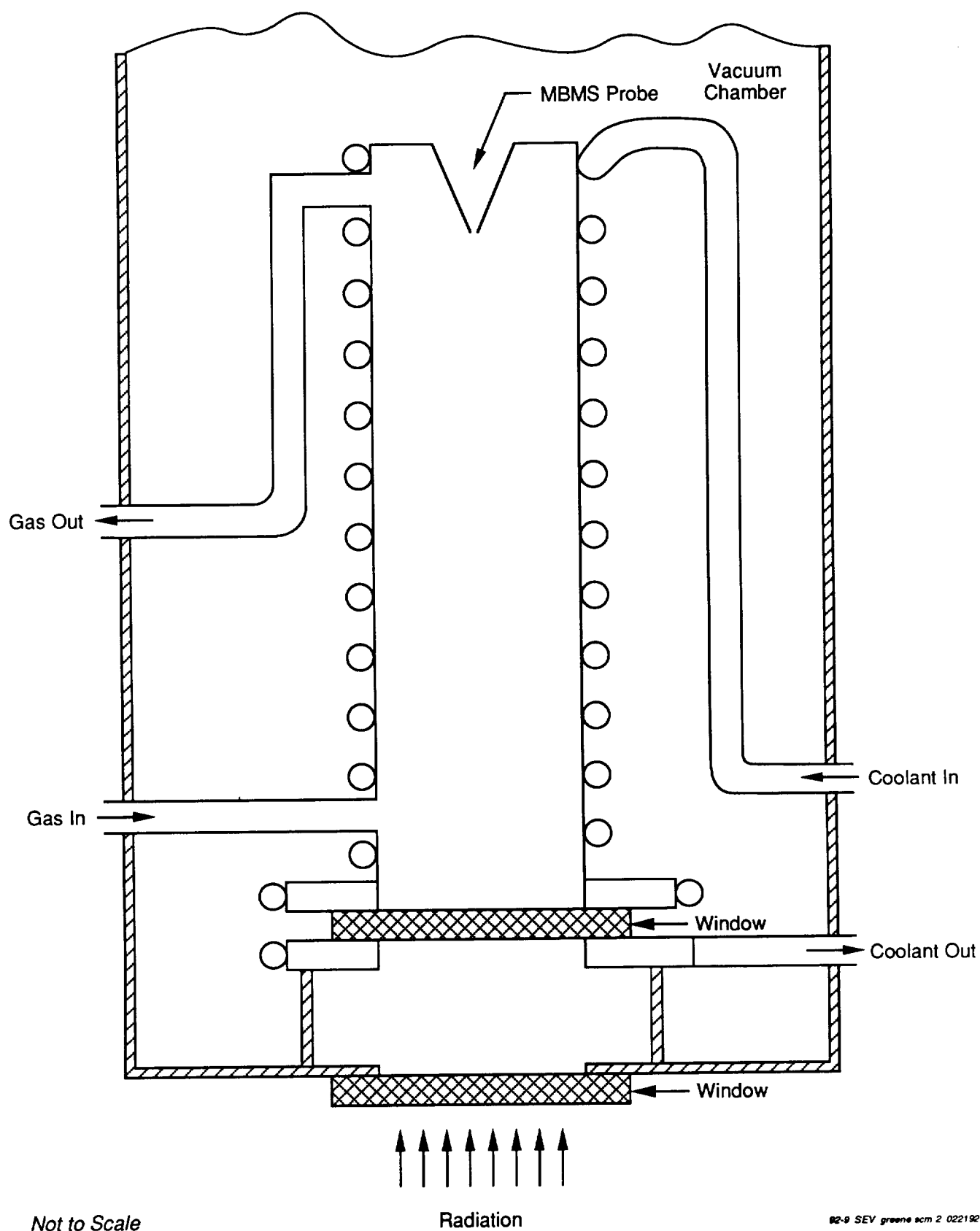
This reactor was used for the initial experiments because of its simple construction and because it permitted changes to be made very rapidly for the investigation of the various chemical systems.

### **The Isothermal Flow Reactor**

The isothermal flow reactor which was used for most of the experiments reported here including the kinetic studies is shown in Figure 3. Many of the elements of this cell are identical to those in the photochemical cell. The most significant difference is the location of the entire cell including the photolysis window inside the vacuum system. This arrangement provides exceptional and very uniform



**Figure 2. The photochemical flow reactor.**



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**Figure 3. The isothermal photochemical flow reactor.**

temperature gradients. The location of the window inside the vacuum chamber eliminates the need for a double window to eliminate external condensation. A heat exchanger was also added so that the gas could be introduced at the cell temperature.

## **SECTION 4**

### **RESULTS**

#### **SURVEY OF CHEMICAL SYSTEMS**

There are a number of chemical systems which have been used for the generation of ClO for kinetic and spectroscopic studies. Several of these systems which appeared to be useful for the identification of ClO dimer and for the kinetic and photolysis studies were investigated. These systems are summarized in Table 1. Primary criteria for the evaluation of these systems included (1) the stability and reproducibility of the system, (2) the maximum concentration of dimer which could be generated, (3) the presence of any competing reactions which could complicate interpretation of the data, and (4) the extent of any mass spectrometric complications.

#### **THE IDENTIFICATION OF CHLORINE-OXYGEN SPECIES**

Molecular beam mass spectrometric techniques were used to search for ClO dimer and any other oxides in all six of the chemical systems cited in Table 1. In addition to the dimer, it was necessary to identify other significant species which might contribute to the mass spectrum of the dimer or which might complicate kinetic and photolysis measurements. The identification of other chlorine oxides, which arguably can be best made by MBMS techniques, is important because they could have a significant role in the chlorine chemistry in the stratosphere.

##### **The Identification of ClO Dimer**

###### **The Mass Spectrum**

The dimer of ClO was generated in six different chemical systems by the combination of ClO radicals in a simple flow reactor operated at total pressures ranging from 5 to 200 torr, temperatures from  $-70^{\circ}$  to  $20^{\circ}\text{C}$  and residence times from 0.04 s to 2 min. The ClO radicals were produced by the reaction of Cl atoms, which were generated by photolysis of  $\text{Cl}_2$ , with  $\text{ClO}_2$ ,  $\text{O}_2$ , or  $\text{Cl}_2\text{O}$ , by the reaction of thermally generated Cl atoms with  $\text{ClO}_2$ , and by the direct photolysis of  $\text{ClO}_2$ . The flow reactor was interfaced to a molecular beam mass

**Table 1. CHEMICAL SYSTEMS STUDIED**

|          |                                     |               |                            |
|----------|-------------------------------------|---------------|----------------------------|
| System 1 | $\text{Cl}_2 + \text{HV}$           | $\rightarrow$ | $\text{Cl} + \text{Cl}$    |
|          | $\text{Cl} + \text{ClO}_2$          | $\rightarrow$ | $\text{ClO} + \text{ClO}$  |
|          | $\text{ClO}_2 + \text{HV}$          | $\rightarrow$ | $\text{ClO} + \text{O}$    |
| System 2 | $\text{Cl}_2 + \text{HV}$           | $\rightarrow$ | $\text{Cl} + \text{Cl}$    |
|          | $\text{Cl} + \text{Cl}_2\text{O}$   | $\rightarrow$ | $\text{Cl}_2 + \text{ClO}$ |
|          | $\text{Cl}_2\text{O} + \text{HV}$   | $\rightarrow$ | $\text{Cl} + \text{ClO}$   |
| System 3 | $\text{Cl}_2 + \text{HV}$           | $\rightarrow$ | $\text{Cl} + \text{Cl}$    |
|          | $\text{Cl} + \text{O}_2 + \text{M}$ | $\rightarrow$ | $\text{ClOO} + \text{M}$   |
|          | $\text{Cl} + \text{ClOO}$           | $\rightarrow$ | $\text{ClO} + \text{ClO}$  |
| System 4 | $\text{Cl}_2 + \Delta$              | $\rightarrow$ | $\text{Cl} + \text{Cl}$    |
|          | $\text{Cl} + \text{ClO}_2$          | $\rightarrow$ | $\text{ClO} + \text{ClO}$  |
| System 5 | $\text{ClO}_2 + \text{HV}$          | $\rightarrow$ | $\text{ClO} + \text{O}$    |
|          | $\text{ClO}_2 + \text{O}$           | $\rightarrow$ | $\text{ClO} + \text{O}_2$  |
| System 6 | $\text{Cl}_2 + \text{HV}$           | $\rightarrow$ | $\text{Cl} + \text{Cl}$    |
|          | $\text{Cl} + \text{O}_3$            | $\rightarrow$ | $\text{ClO} + \text{O}_2$  |



spectrometric system which incorporated both a large magnetic mass spectrometer with high resolution capabilities and a quadrupole mass spectrometer, and which utilized beam modulation and phase sensitive detection. This system, which was optimized for operation at pressures up to 1 atm and which had a detection limit of better than 1 ppb, was used to obtain mass spectra of the reaction products. In addition to the expected signals for reactants and ClO radicals, strong signals were also obtained at  $m/e = 102$ , 104 and 106. A typical scan is shown in Figure 4. This scan, which was obtained with a short, 1 s time constant without any signal averaging, indicates the excellent signal-to-noise which can be obtained. These peaks were assigned to the dimer of ClO based on: (1) mass to charge ratio, (2) the excellent agreement between the observed and calculated isotope ratios, (3) the fact that the ions were only observed in the presence of light in the photolysis experiments or when the furnace temperature was great enough to dissociate  $\text{Cl}_2$  in the thermal experiments, and (4) the ratio of ClO dimer to ClO was only weakly dependent on reactor pressure suggesting that it was not being produced in the initial beam forming process during sampling.

#### Velocity Analysis Measurements

The mass spectrometric identification of the ClO dimer was further supported by time-of-flight velocity analyses. Velocity distributions were obtained for the neutral precursor of the mass spectrometric peak observed at  $m/e = 102$  and for the peaks produced by several other known species. Some typical distributions of flight times of species in the molecular beam, at 40 torr and  $-40^\circ\text{C}$ , are given in Figure 5. These distributions showed that the neutral precursor of  $\text{Cl}_2\text{O}_2^+$  has a nominal mass of 102 amu. Furthermore, considering the shift of the peaks with molecular weight, these data show that  $\text{Cl}_2\text{O}_2^+$  cannot be a fragment from a significantly larger molecule, such as one containing one or more additional chlorine or oxygen atoms. Since the only major gaseous elements present in the system are chlorine, oxygen and nitrogen, these data provide unequivocal proof of the existence of ClO dimer.

#### Diagnostic Measurements

Dimers and higher clusters can be formed during noneffusive expansions, even at relatively large Knudsen numbers.<sup>15</sup> It was therefore essential to show that the ClO dimer observed was not an artifact of the molecular beam formation process. Generally the most convenient method of determining the contribution of any reactions in a free-jet to the species observed in a molecular beam is by varying the size of the expansion aperture. The number of collisions which occur during a free-jet expansion is, to a first order approximation, proportional to the diameter of a circular orifice. Consequently, it is possible to determine the extent

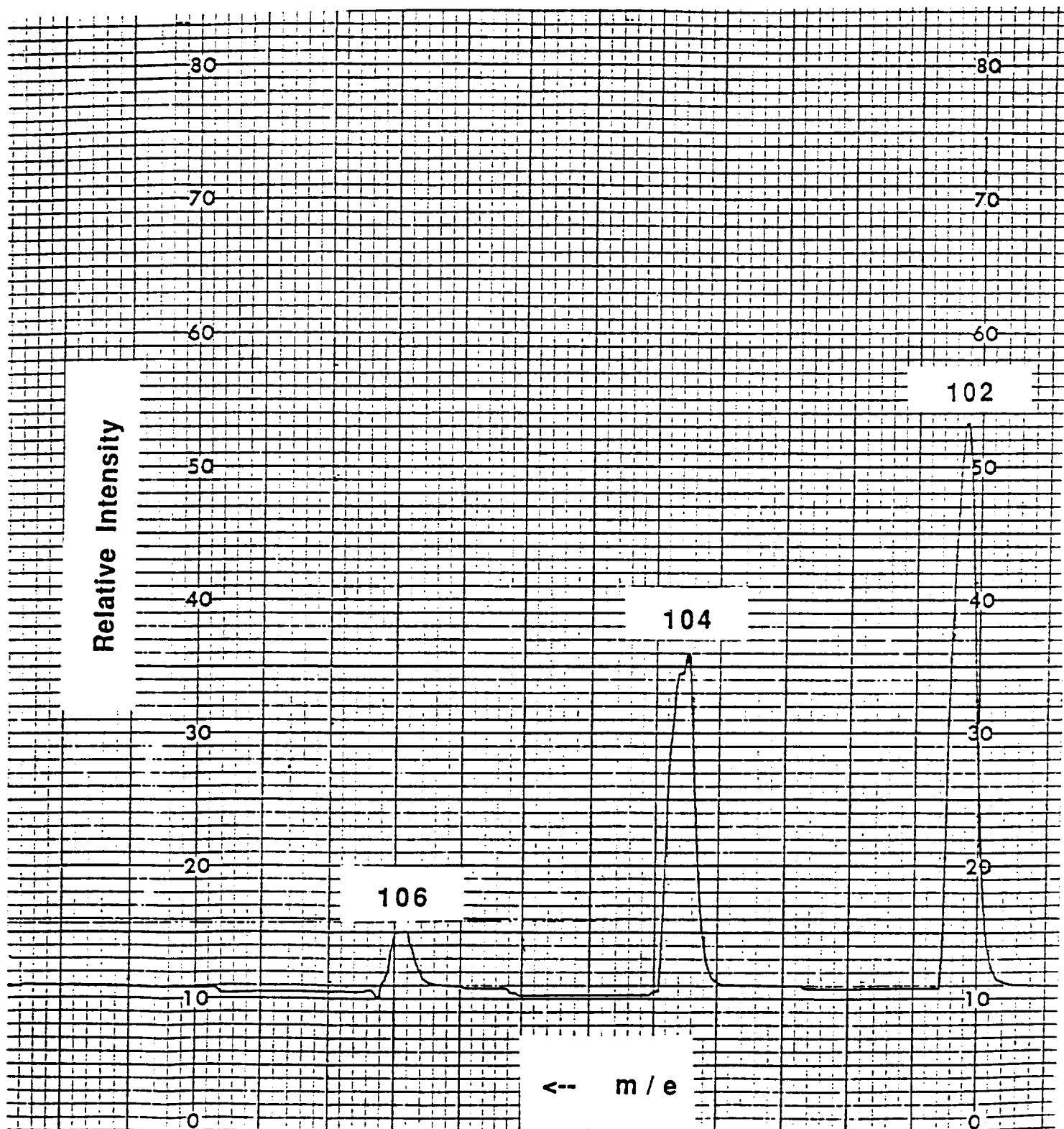
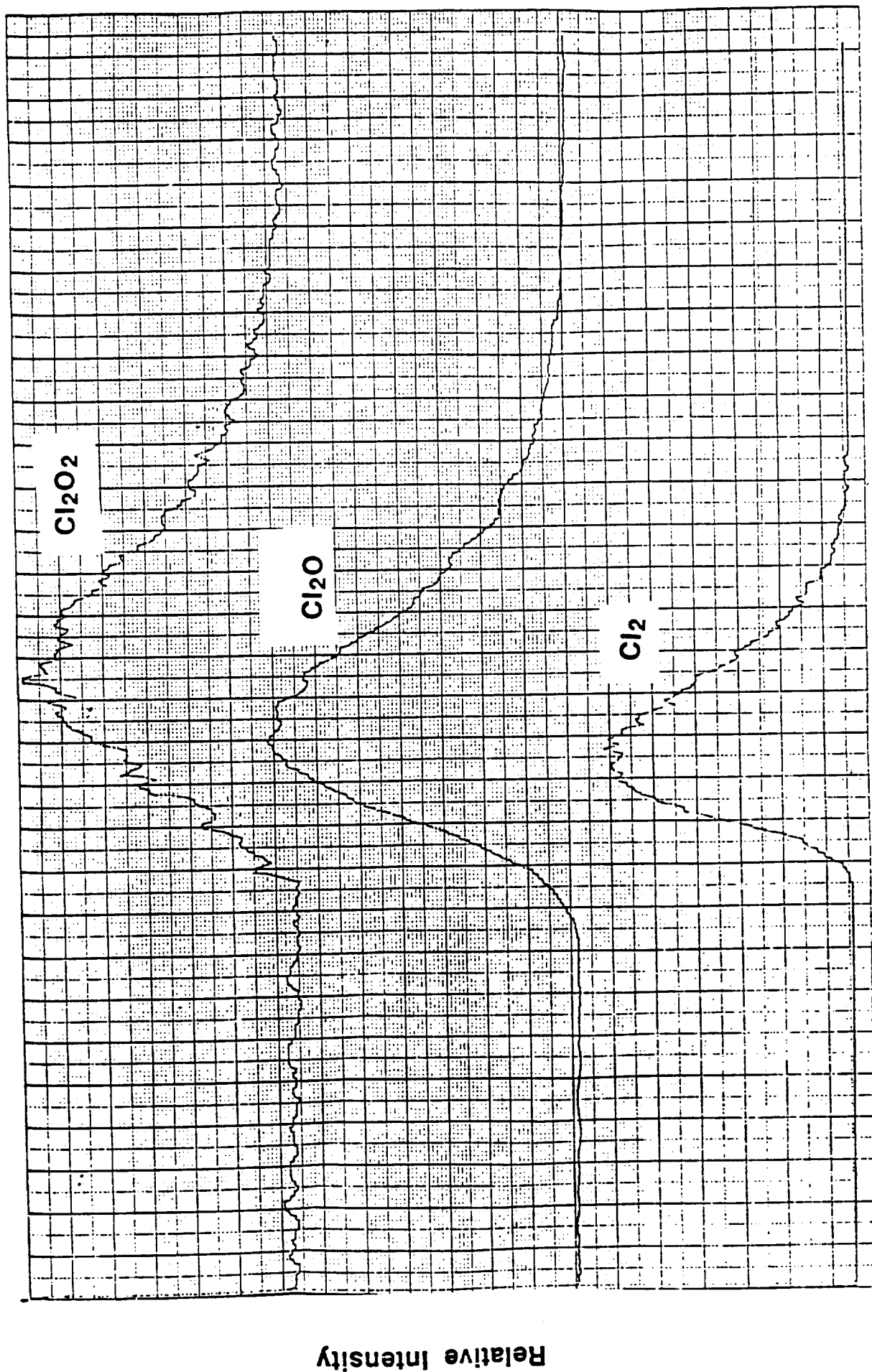


Figure 4. Scan of the mass spectrometric peaks assigned to ClO dimer.



Time

Figure 5. Time-of-arrival curves for ClO dimer, Cl<sub>2</sub>O, and Cl<sub>2</sub>.

Relative Intensity

of reactions in the expansion and often to make corrections simply by measuring ratios of species in the beam as a function of the orifice size.<sup>16</sup> The number of collisions is also a function of the total and partial pressures, but the interpretation of the dependencies is much more complex, particularly in cases such as dimer formation which involve three body processes in multicomponent systems.

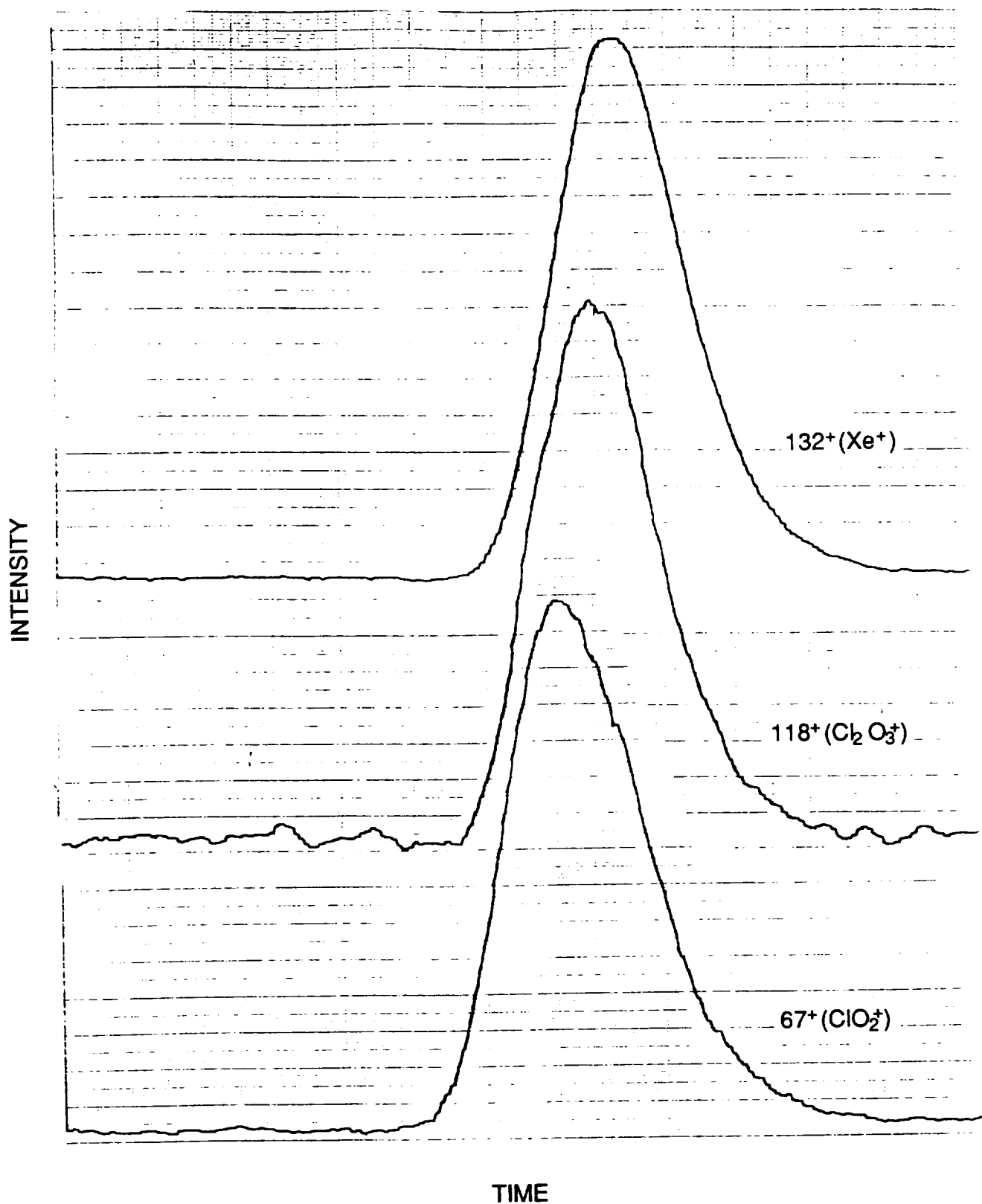
Measurements were made of the ratios of ClO dimer to monomer using various sampling orifices with diameters from 12 to 100 micrometers, total pressures from 30 to 760 torr, and chemical systems 1 to 4 (see Table 1). These data indicated that the relative dimer concentrations were largely independent of the pressure and sampling orifice diameter, but the results were not definitive because the concentrations of reactants could not be reproduced with sufficient precision. Since the reacting systems were stable, a cell was designed in which the sampling orifice could be changed in-situ in a few seconds. This cell, however, was not constructed because the question was definitively resolved by the transient measurements discussed below (see Figures 7 through 17). At the beginning of the laser induced reaction the concentration of ClO is very high but the concentration of dimer is negligible. Consequently, there can be no significant dimerization occurring in the beam-forming expansion. The variable-orifice cell will probably be needed for proposed studies of Cl<sub>2</sub>O<sub>3</sub> and the other Cl-O species.

### **The Identification of Cl<sub>2</sub>O<sub>3</sub>**

In chemical systems containing both ClO<sub>2</sub> and ClO peaks in the mass spectrum were always observed at  $m/e = 118, 120$  and  $122$ . The relative peak intensities were those of a species containing two chlorine atoms, and so the ions were assigned to Cl<sub>2</sub>O<sub>3</sub><sup>+</sup>. Results of velocity analysis of the neutral precursor of Cl<sub>2</sub>O<sub>3</sub><sup>+</sup> are shown in Figure 6. The resolution obtained in this velocity analysis, even at this relatively high pressure, shows that the neutral precursor of 118+ has a mass which cannot differ by as much as an oxygen atom or chlorine atom from that of Cl<sub>2</sub>O<sub>3</sub>. Consequently, the observed ion cannot be a fragment from a larger chlorine oxide, and so the neutral precursor of 118+ can be positively identified as Cl<sub>2</sub>O<sub>3</sub>. The identification is also supported by the dependence of the 118+ on the concentrations ClO and Cl<sub>2</sub>. The presence of this adduct in this system was previously suggested by Cox et al.<sup>8</sup> and Burkholder et al.<sup>7</sup>

### **Measurements of Higher Oxides**

The presence or absence of other chlorine oxides in both the atmosphere and in laboratory systems is of considerable importance. The higher oxides have been proposed as a reservoir of active chlorine in the Antarctic stratosphere during



**Figure 6.** Time-of-arrival curves for  $\text{Cl}_2\text{O}_3$ ,  $\text{ClO}_2$  and xenon. The xenon was introduced into the reaction mixture as a high mass reference.

early spring, and may also be a cause of the poor chlorine balances obtained in some atmospheric studies.

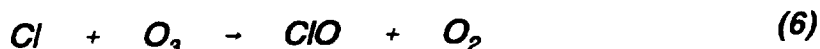
A limited series of experiments directed toward the determination of the presence and relative concentrations of other Cl-O species in both ClO<sub>2</sub>/Cl<sub>2</sub> mixtures and Cl<sub>2</sub>/O<sub>3</sub> under typical stratospheric conditions was carried out at temperatures of -40° to -60°C and pressures of 30 to 760 torr. Under these conditions only small concentrations of higher oxides were observed in the ClO<sub>2</sub>/Cl<sub>2</sub> system. No higher oxides were detected in the Cl<sub>2</sub>/O<sub>3</sub> system. These results are summarized in Table 2.

## KINETICS OF THE ClO SELF REACTION AND RATE OF FORMATION OF ClO DIMER

The kinetics of the ClO self reaction and the rate of dimer formation were investigated over a range of temperatures and pressures relevant to the Antarctic stratosphere by time resolved mass spectrometric detection of both ClO radicals and the Cl<sub>2</sub>O<sub>2</sub> dimer produced in the laser photolysis of Cl<sub>2</sub>/O<sub>3</sub> mixtures.

### Procedure

ClO radicals were generated from the laser photolysis of Cl<sub>2</sub>/O<sub>3</sub> mixtures at 355 nm by the following reaction sequence.



The rate of ClO production by this scheme is known to be at least 2 to 3 orders of magnitude faster than the subsequent rate of removal by the self reaction of ClO.<sup>13</sup> Hence the rate of ClO generation need not be considered in the kinetic analysis. The rate of ClO self reaction was determined from mass spectrometric measurements of the rate of disappearance of ClO and compared with measurements of the rate of formation of the dimer.

A 1% mixture of Cl<sub>2</sub> and O<sub>3</sub> in an O<sub>2</sub> buffer gas is flowed under "slow flow conditions" through a heat exchanger and into the low temperature photolysis cell. The gas mixture is then photolyzed with 355 nm radiation from the frequency tripled output of a Nd:YAG laser operated in the single pulse mode at

**Table 2. RELATIVE INTENSITIES OF MASS SPECTROMETRIC SIGNALS OBSERVED IN PHOTOLYZED ClO<sub>2</sub>-Cl<sub>2</sub> MIXTURES AT 50 TORR AND -40°C**

| Possible species                 | m/e             | Relative intensity |
|----------------------------------|-----------------|--------------------|
| O <sub>2</sub> +                 | 32              | 56444              |
| ClO+                             | 51              | 130                |
| ClO <sub>2</sub> +               | 67 <sup>a</sup> | 7393               |
| Cl <sub>2</sub> +                | 70              | 355                |
| ClO <sub>3</sub> +               | 83              | 41                 |
| Cl <sub>2</sub> O+               | 86              | 76                 |
| ClO <sub>4</sub> +               | 99              | ND <sup>b</sup>    |
| Cl <sub>2</sub> O <sub>2</sub> + | 102             | 72                 |
| Cl <sub>2</sub> O <sub>3</sub> + | 118             | 450                |
| Cl <sub>2</sub> O <sub>4</sub> + | 134             | 73                 |
| Cl <sub>2</sub> O <sub>6</sub> + | 166             | Trace              |
| Cl <sub>2</sub> O <sub>7</sub> + | 182             | ND <sup>b</sup>    |
| Cl <sub>2</sub> O <sub>8</sub> + | 198             | ND <sup>b</sup>    |

<sup>a</sup> Corresponds to 50% decomposition.

<sup>b</sup> Not Detectable.

a repetition rate of 12 s per pulse. Total gas flow rates were adjusted to provide a residence time in the cell of ~ 7 to 10 s. In this way reactants and photolysis products remaining from any previous laser pulse are swept from the cell and replaced with unirradiated reactants before the next laser pulse. The resulting mixture of reactants and products are continuously sampled by an orifice at the end of the cell leading directly into the MBMS system.

Temporal profiles were measured for both  $\text{ClO}^+$  and  $\text{Cl}_2\text{O}_2^+$  using the Nuclide mass spectrometer. Ion signals were output to a V/F converter and then to a multichannel analyzer. The mass spectrometer, laser, and the multichannel analyzer were all controlled by a series of pulse generators to synchronize the timing sequence of the experiment. The timing sequence was set up as follows: (1) the mass spectrometer was set to monitor  $m/e = 51^+$ , (2) a four second delay was then allowed in order for the magnet to stabilize, (3) the laser was then triggered, (4) a photodiode on the laser output then triggered the multichannel analyzer, and (5) the mass spectrometer was then reset to the next ion  $m/e = 102^+$  and then the sequence repeats. A period of ~ 12 s between measurements was typical. This allowed sufficient time for the reactants in the cell to be replenished before the next laser pulse.

The data accumulation time of the multichannel analyzer was 1 ms per channel acquired over 512 channels for a total acquisition time of 0.512 s after each laser pulse. These data were accumulated and averaged over at least 500 laser shots per species to improve signal to noise.

## Data

Typical outputs from the multichannel analyzer for the temporal profiles measured for  $51^+$  and  $102^+$  are presented in Figures 7a through 17a. Measurements were made at several temperatures between  $-20^\circ$  and  $-70^\circ\text{C}$  and pressures ranging from 30 to 117 torr. As was previously discussed the ion signal at  $102^+$  has been identified as the molecular ion of the dimer. The ion at  $51^+$  corresponds to a combination of both the molecular ion of  $\text{ClO}$  and a fragment ion from the dimer. To extract a profile due only to  $\text{ClO}$  radicals the contribution from the dimer must be subtracted. The fragmentation pattern of the dimer was examined and measurements made of the ratio of the ion signals  $I^{51^+}/I^{102^+} = 4.02$  at 40 ev. Thus the measured ion signal for  $102^+$  can be used to calculate the contribution to  $51^+$  from the dimer. Compared in Figures 7b through 17b are typical plots of the total ion signal at  $51^+$  with the  $51^+$  signal calculated from the  $102^+$  ion signal corresponding to the fragment ion from the dimer. These two curves are subtracted to yield the signal due only to  $\text{ClO}$  radicals as shown in Figures 7c through 17c.



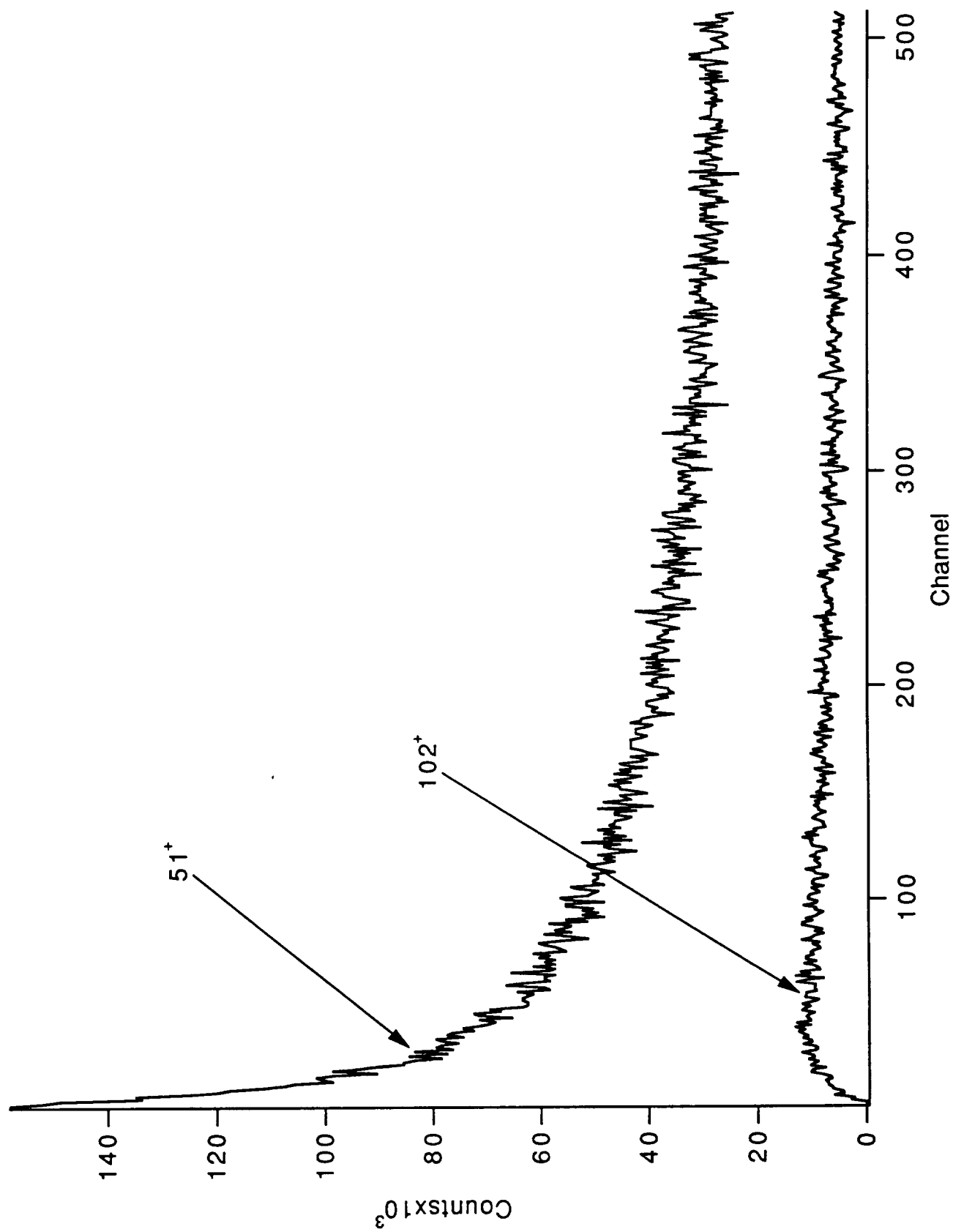
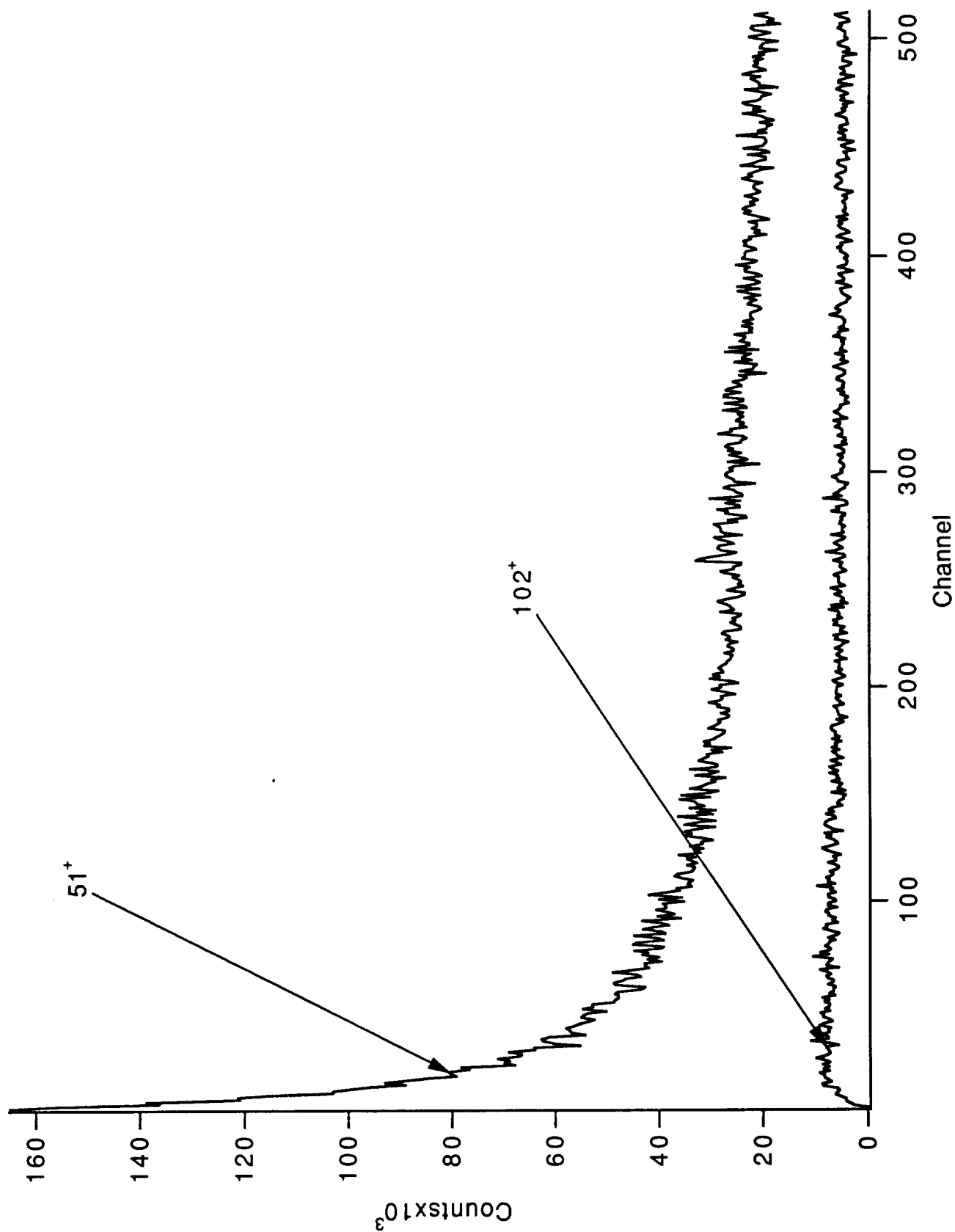
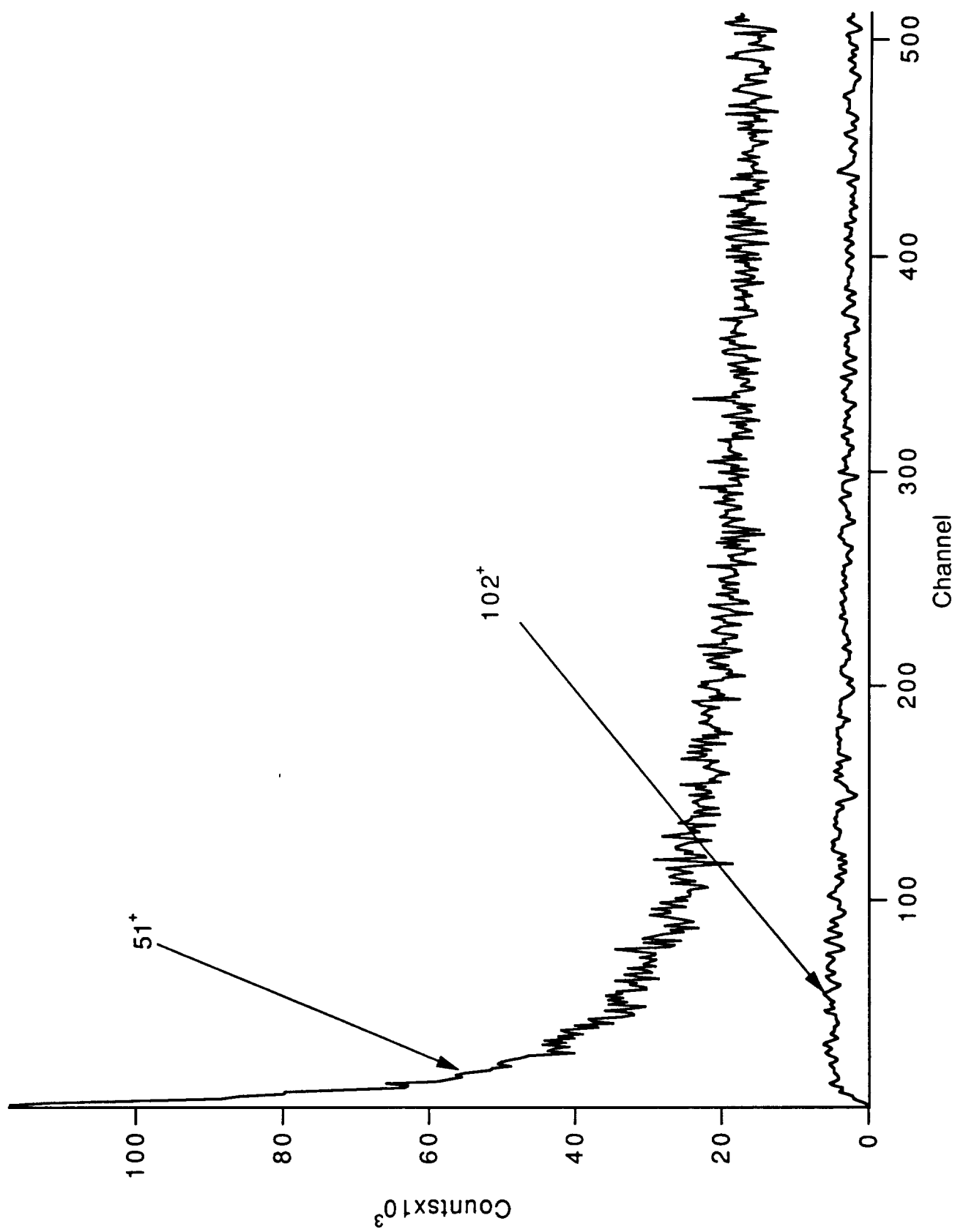


Figure 7a. Multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 78 torr and  $-49^\circ\text{C}$ .



**Figure 8a.** Direct multichannel analyzer outputs for  $51^+$  and  $102^+$  measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 77 torr and  $-40^\circ\text{C}$ .



**Figure 9a.** Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a Cl<sub>2</sub>/O<sub>3</sub> mixture at 75 torr and -67°C.

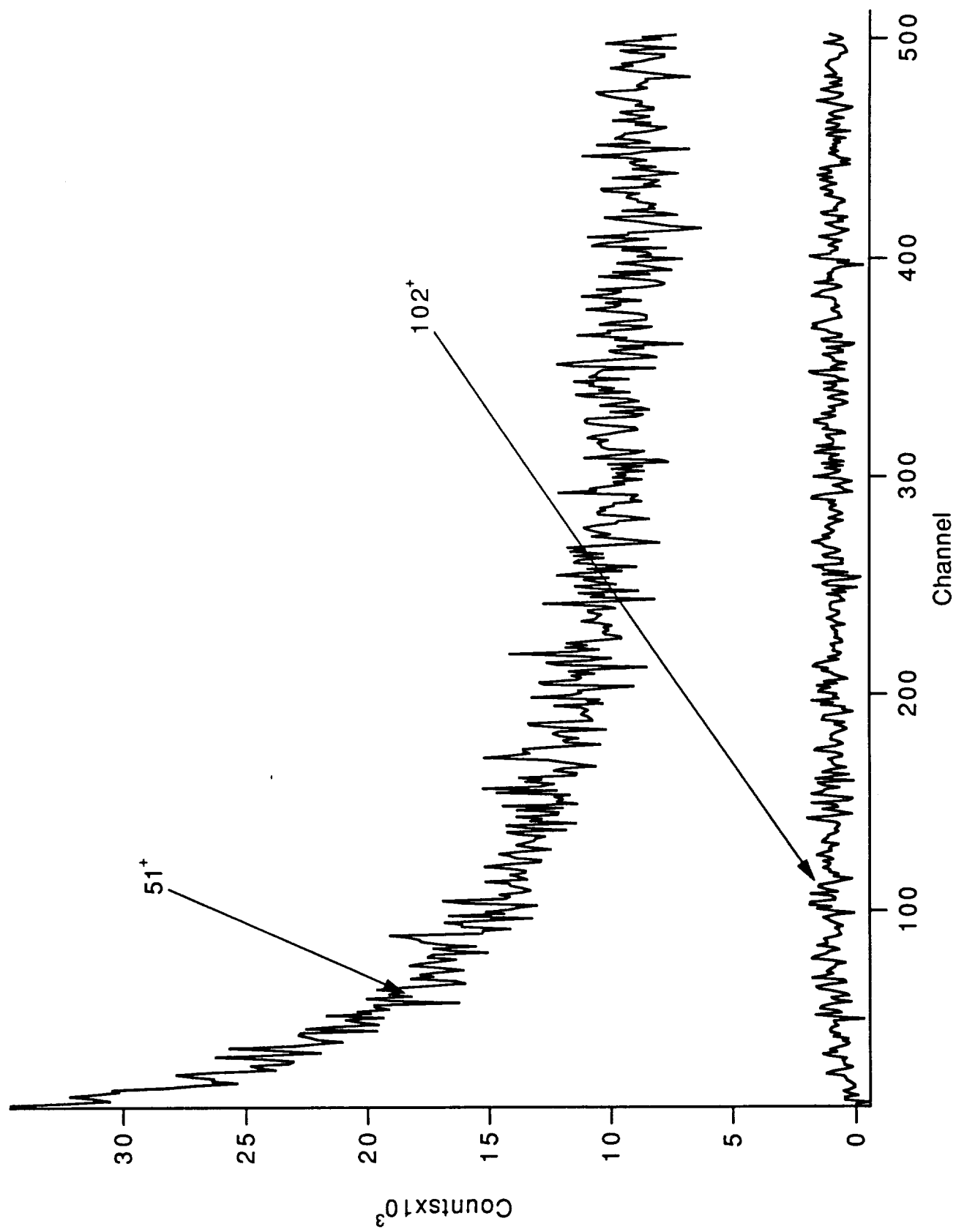


Figure 10a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 30 torr and  $-67^\circ\text{C}$ .

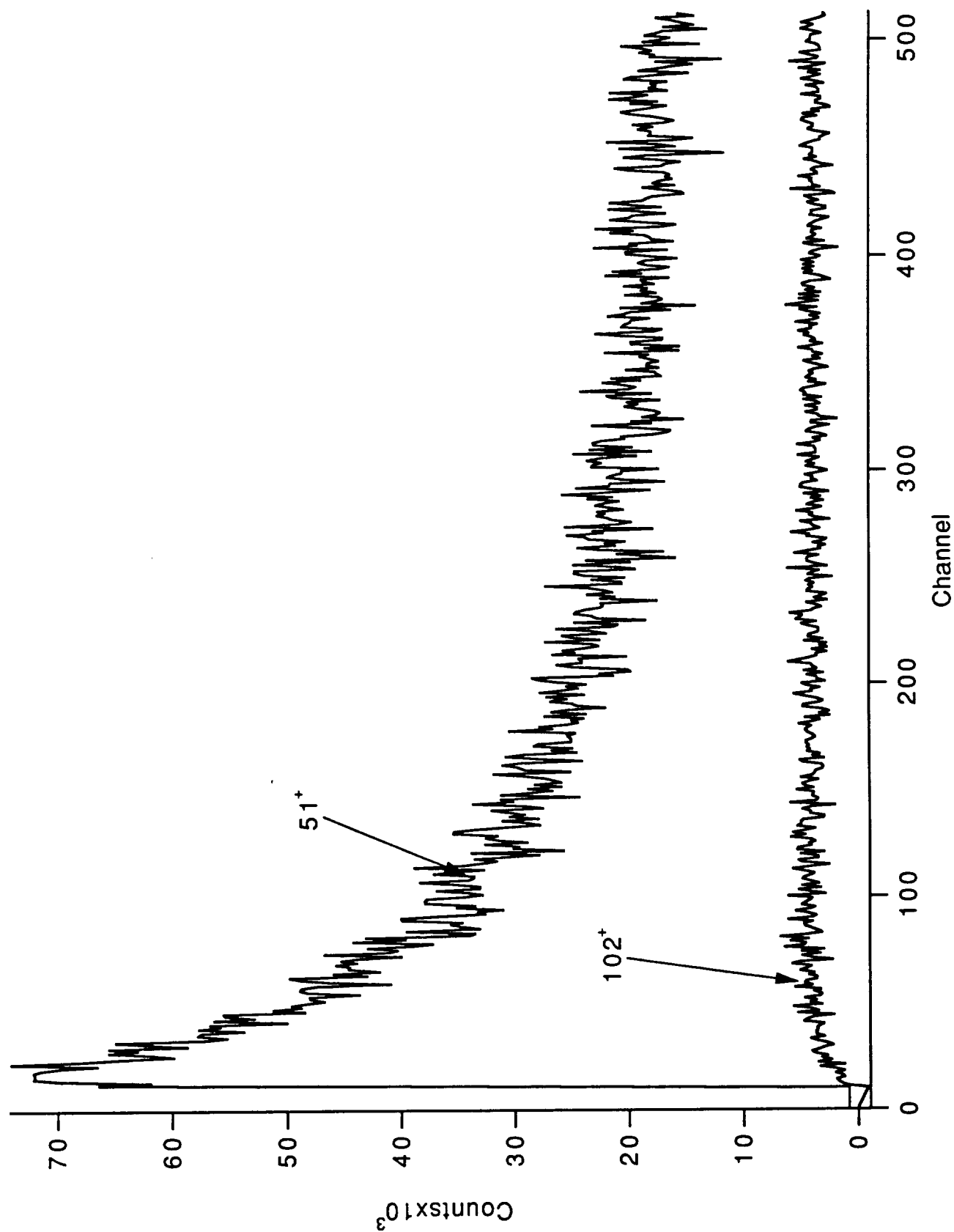


Figure 11a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 32 torr and  $-65^\circ\text{C}$ .

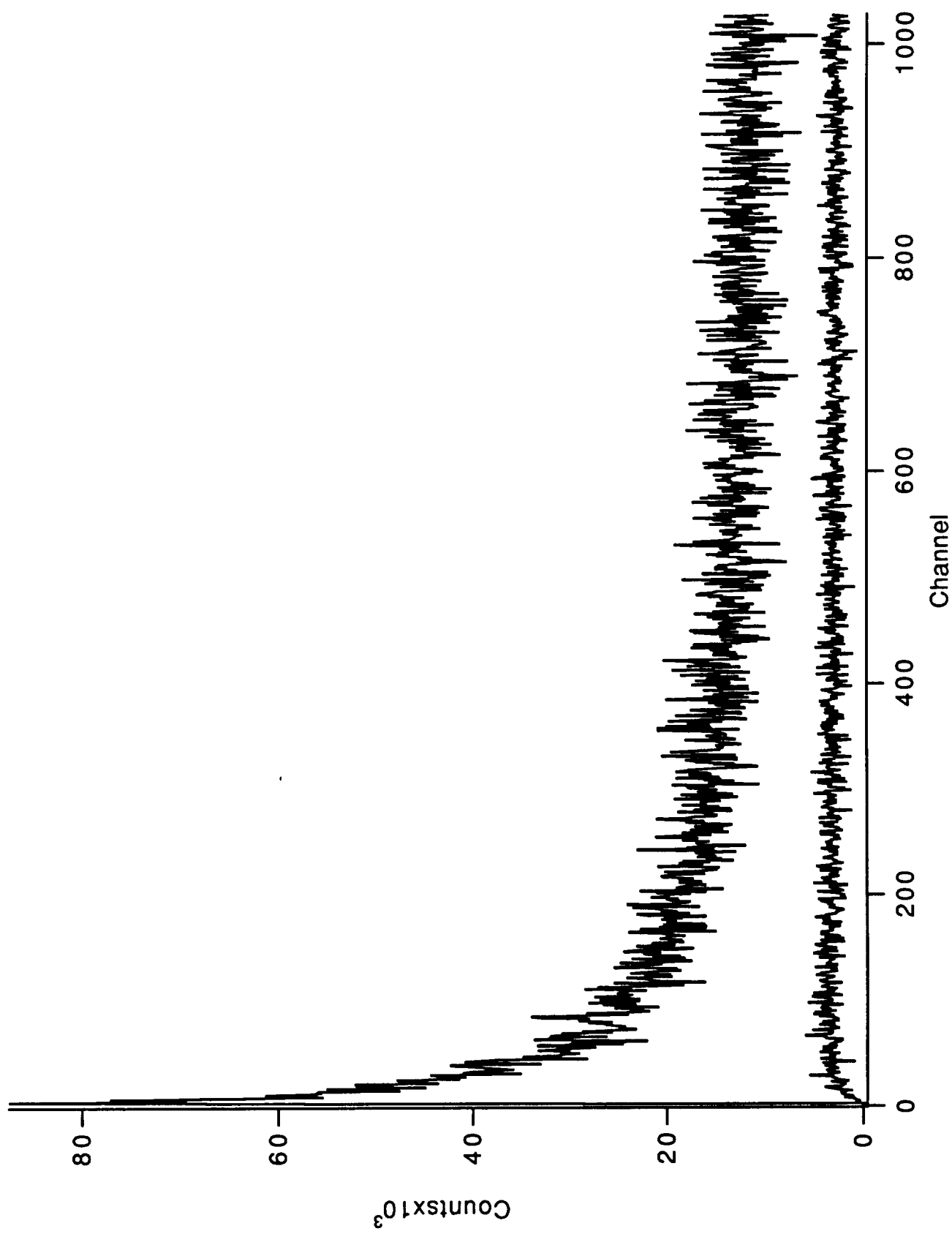


Figure 12a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 78 torr and  $-40^\circ\text{C}$ .

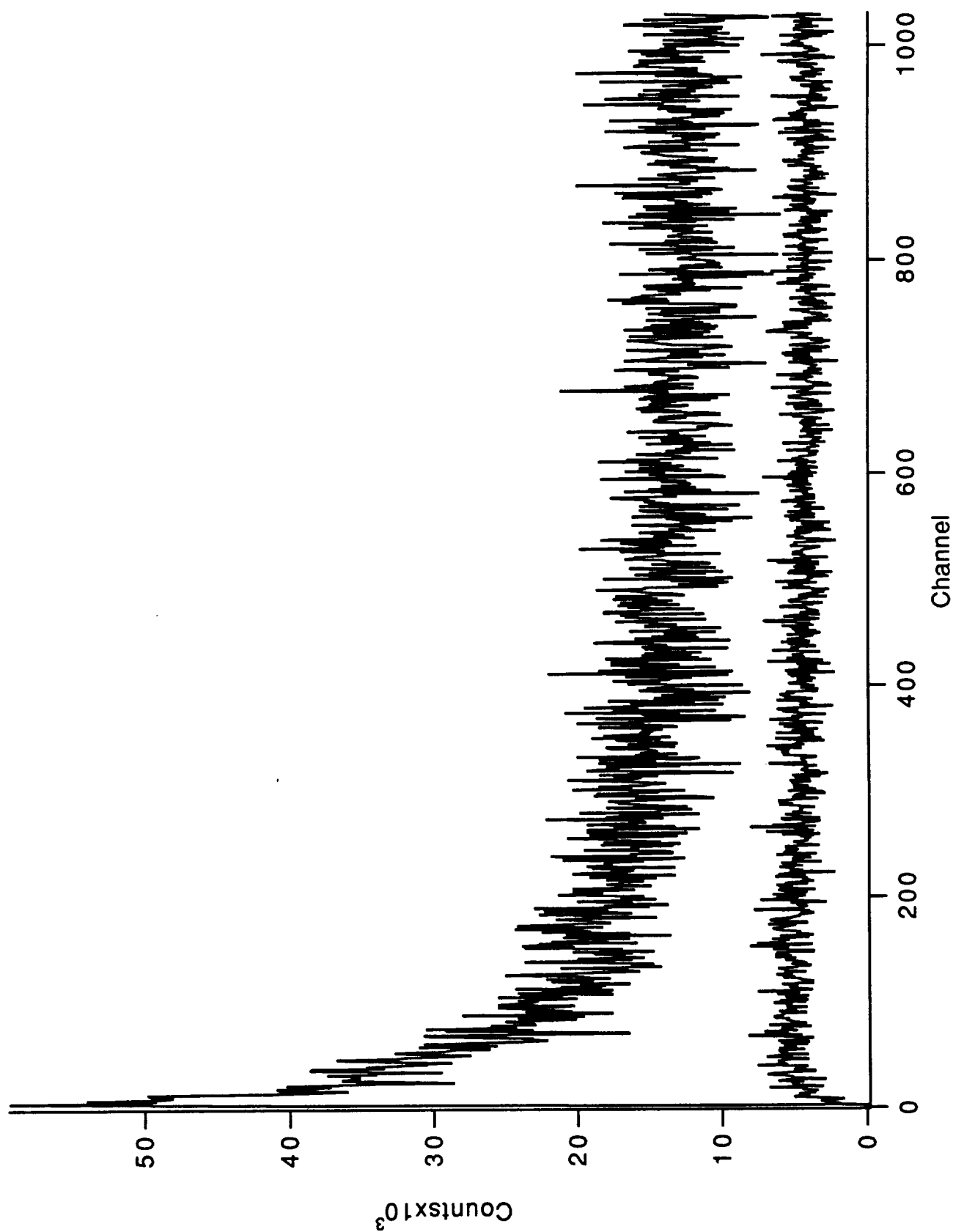


Figure 13a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 78 torr and  $-56^\circ\text{C}$ .

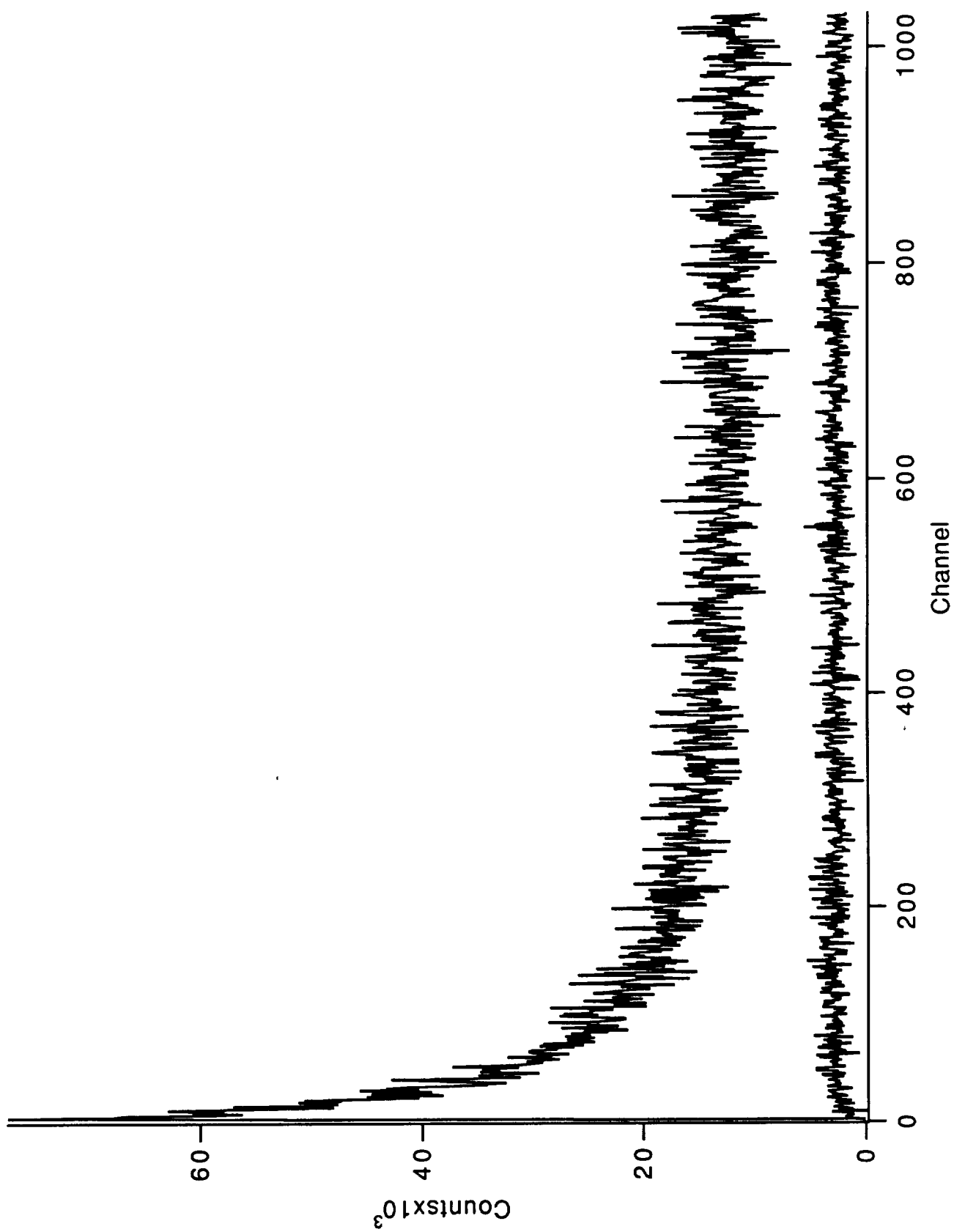


Figure 14a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 75 torr and  $-20^\circ\text{C}$ .



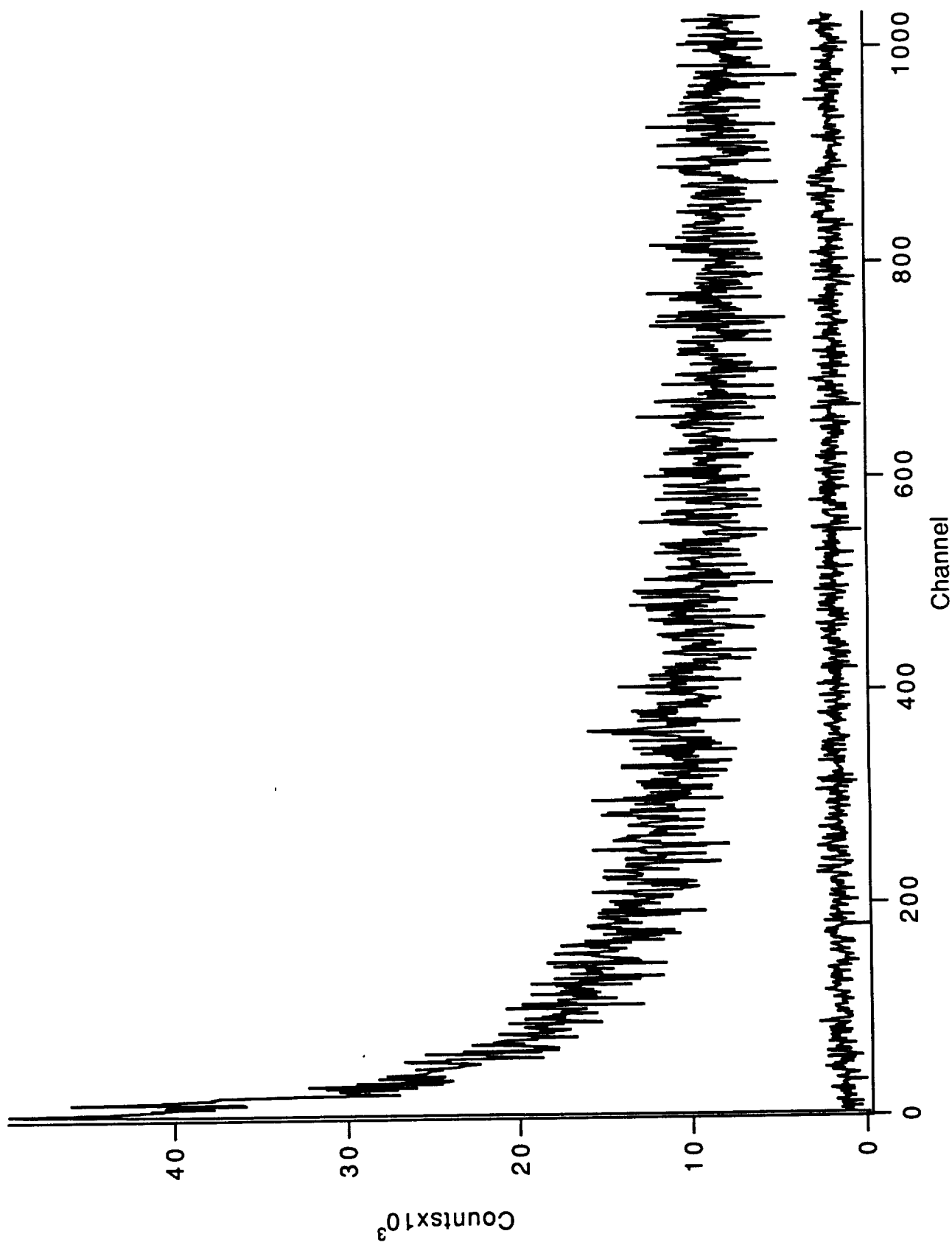


Figure 15a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 30 torr and  $-40^\circ\text{C}$ .

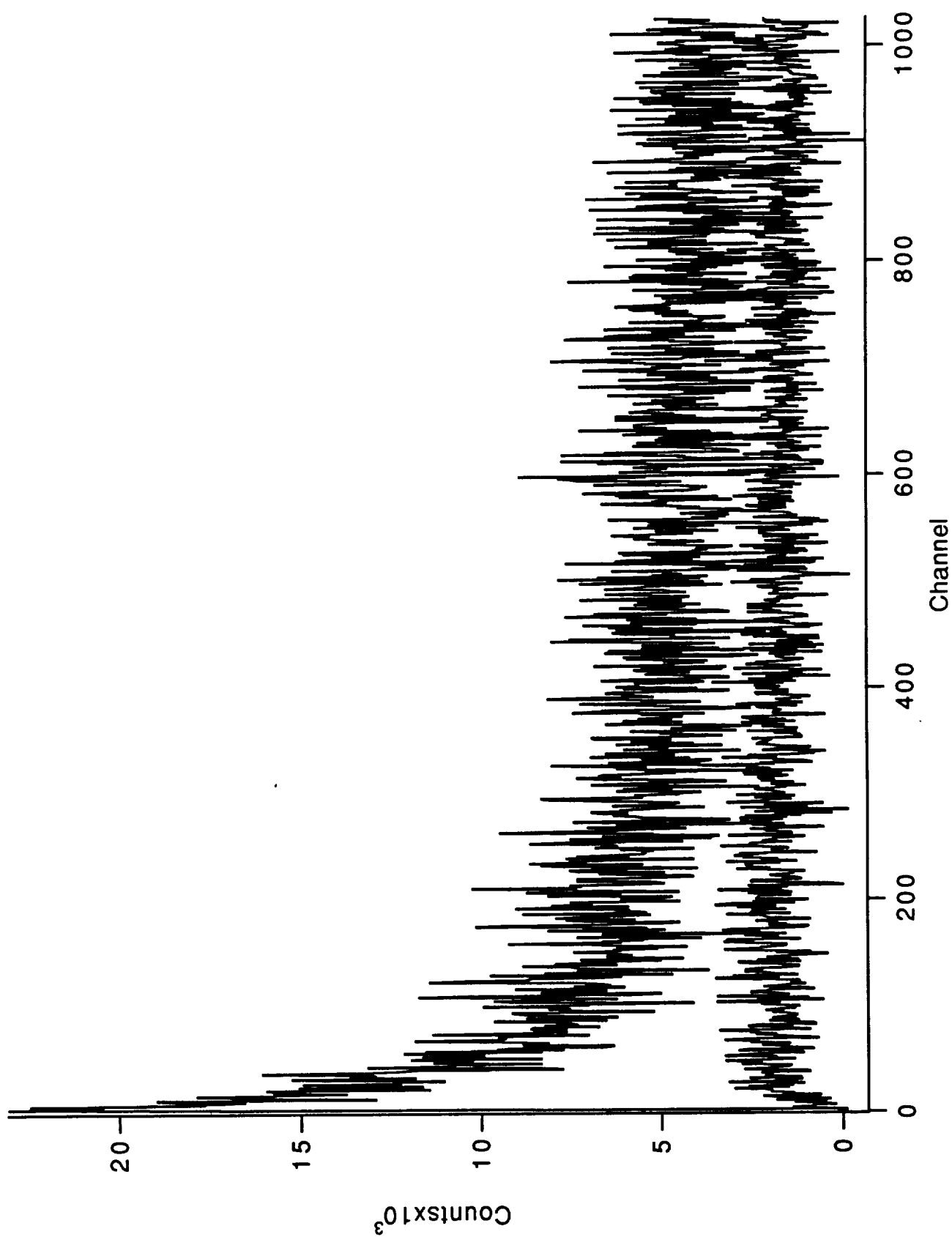


Figure 16a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 78 torr and  $-70^\circ\text{C}$ .

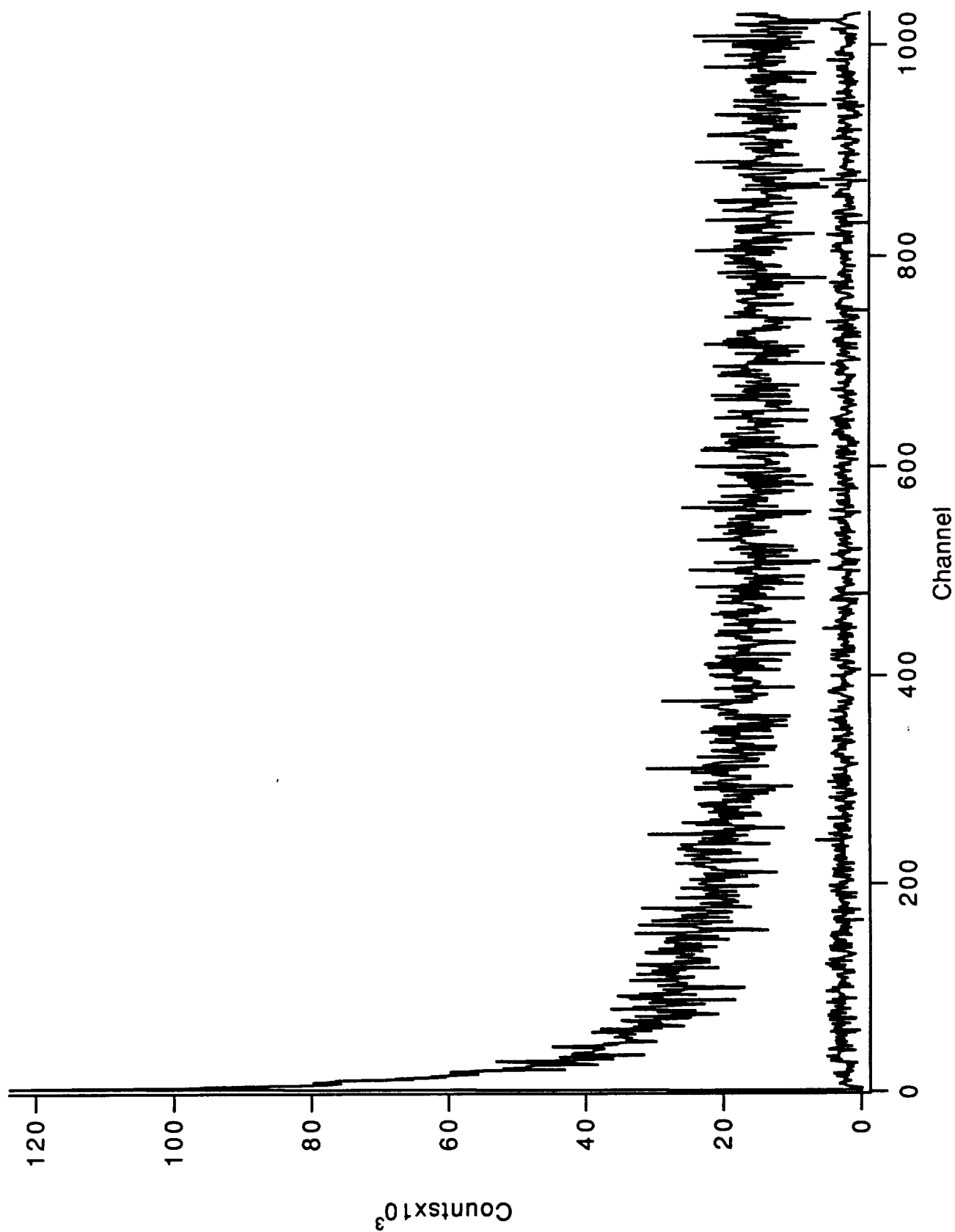


Figure 17a. Direct multichannel analyzer outputs for 51+ and 102+ measured after laser photolysis of a  $\text{Cl}_2/\text{O}_3$  mixture at 120 torr and  $-40^\circ\text{C}$ .

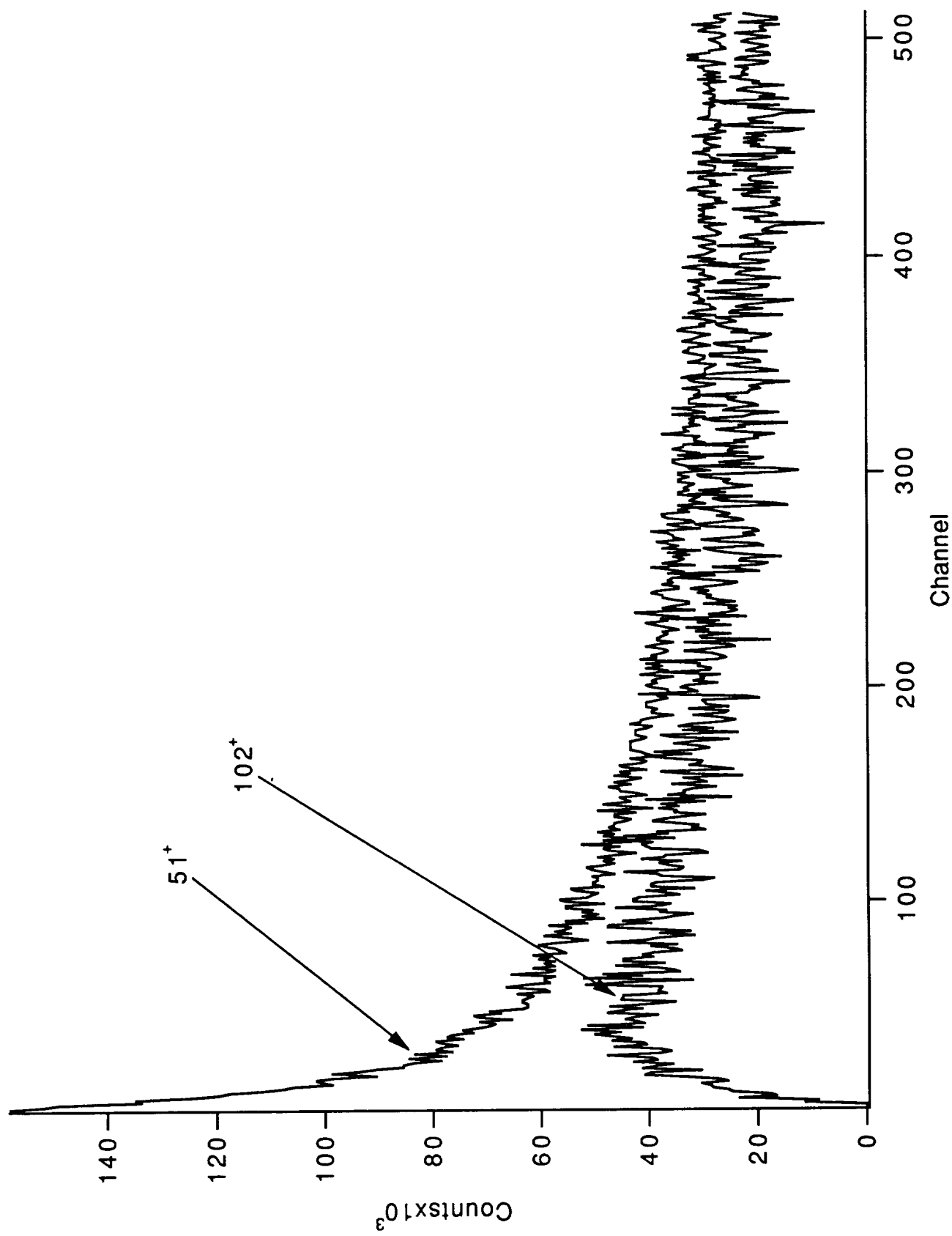


Figure 7b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of  $\text{Cl}_2\text{O}_2$ .

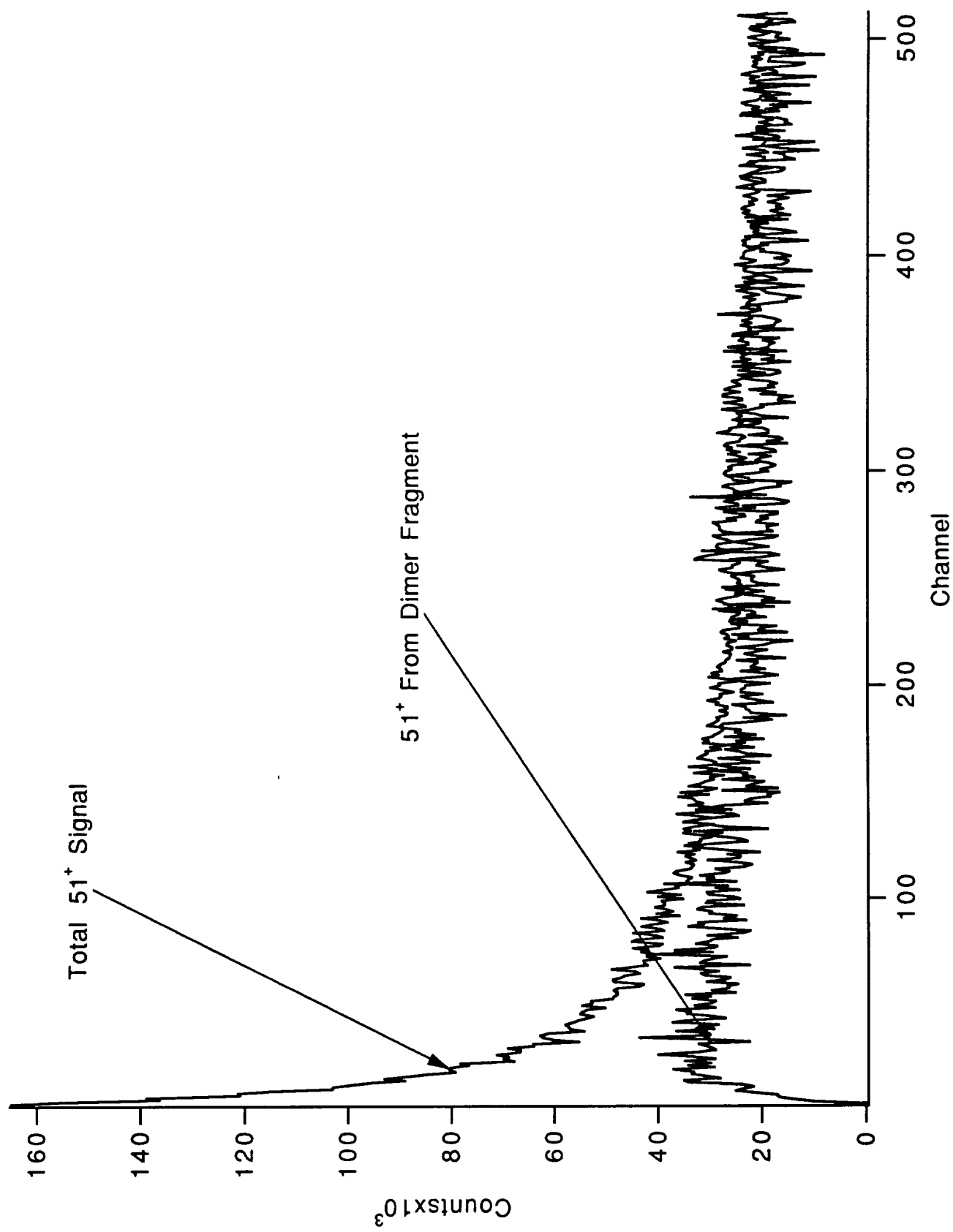


Figure 8b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of Cl<sub>2</sub>O<sub>2</sub>.

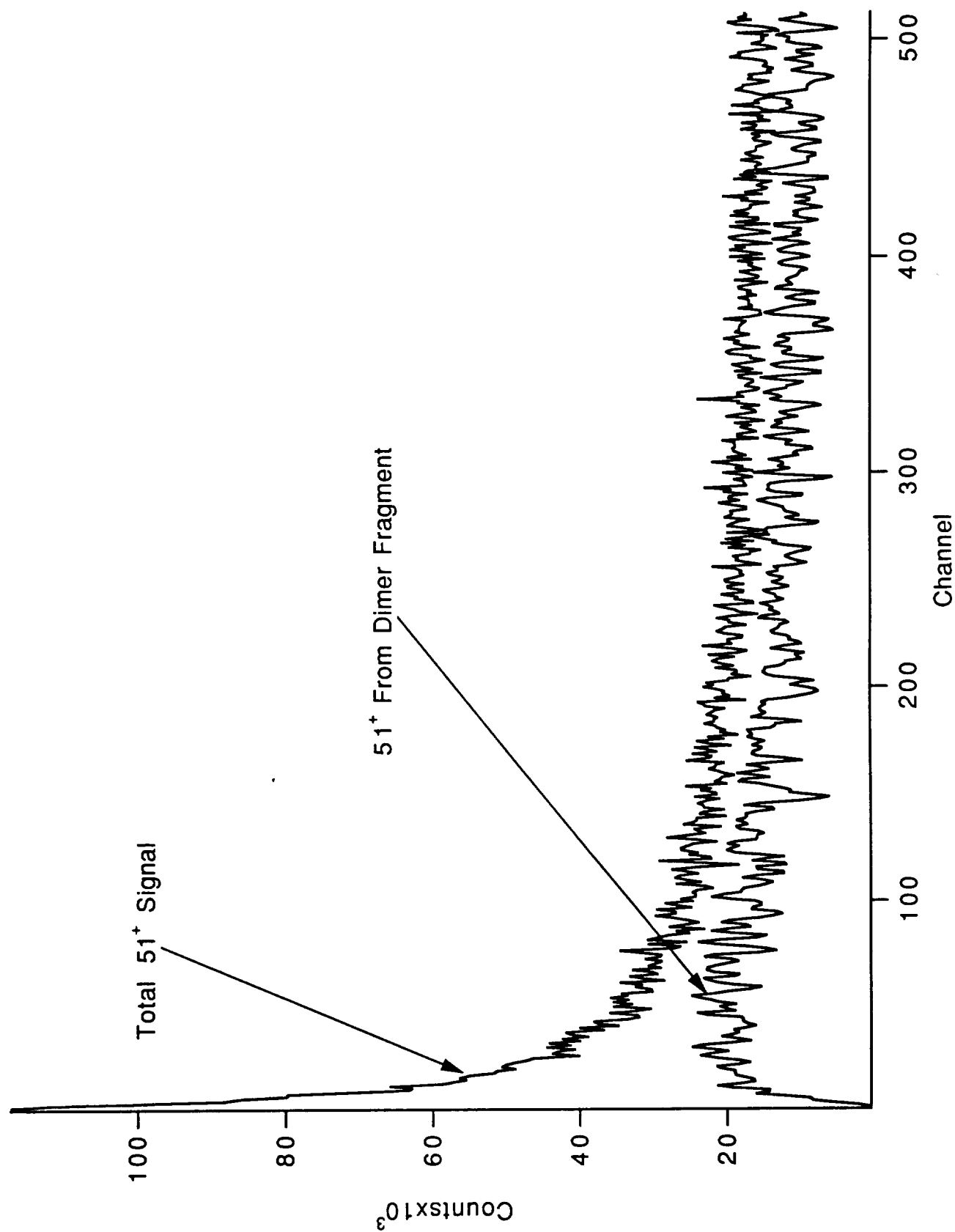


Figure 9b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of Cl<sub>2</sub>O<sub>2</sub>.

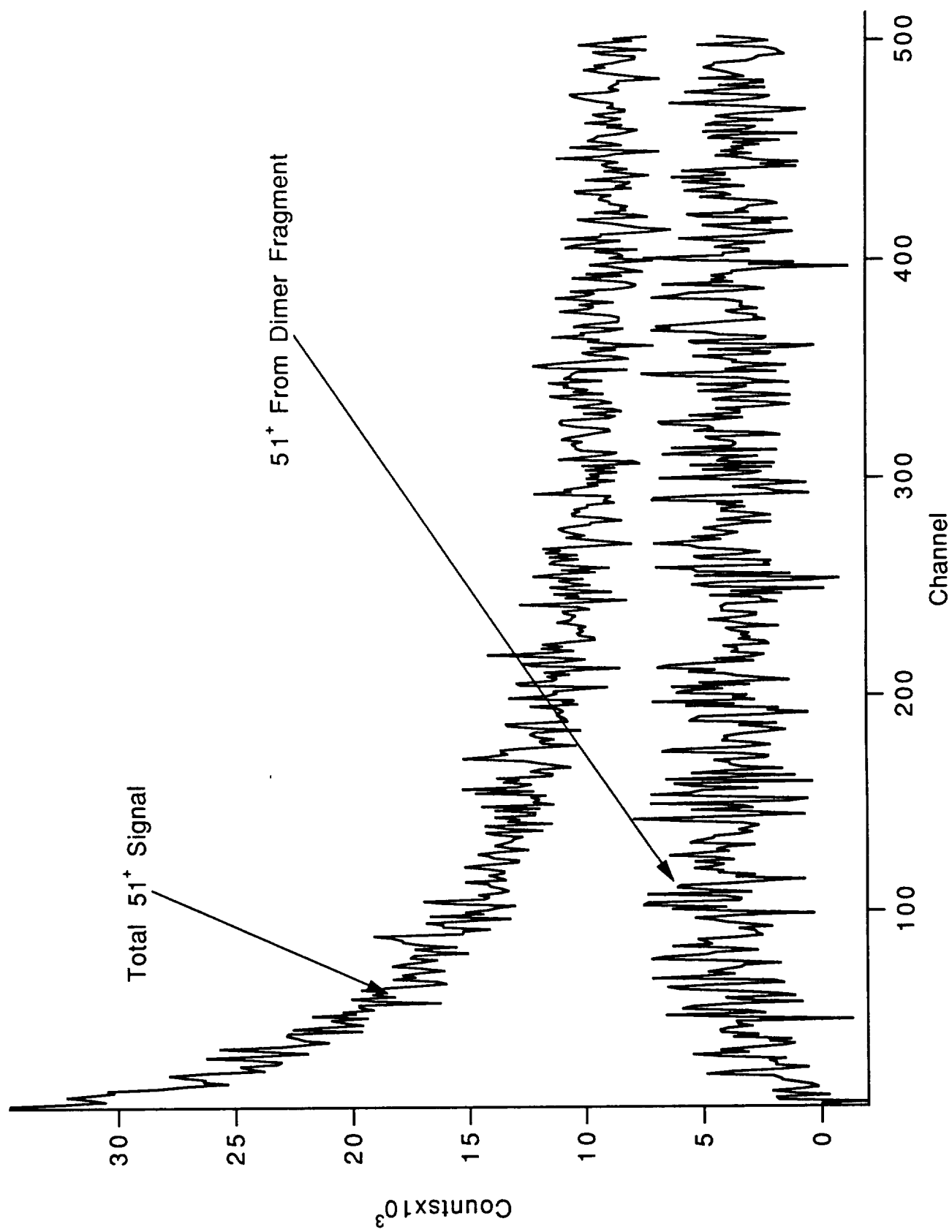
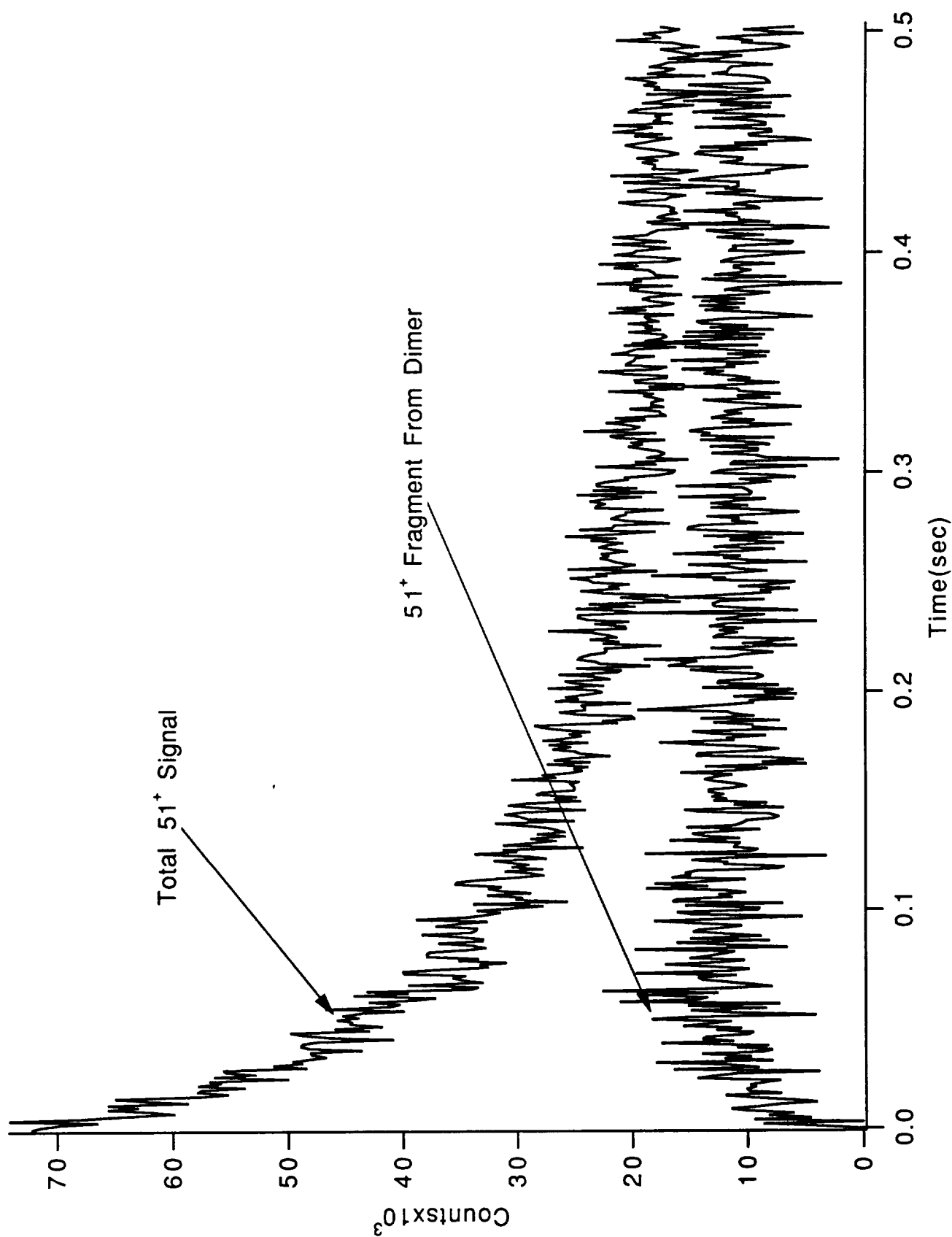


Figure 10b. Multichannel analyzer output for  $51^+$ . Bottom curve is the contribution to  $51^+$  from the fragment ion of  $\text{Cl}_2\text{O}_2^-$ .



**Figure 11b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of Cl<sub>2</sub>O<sub>2</sub>.**



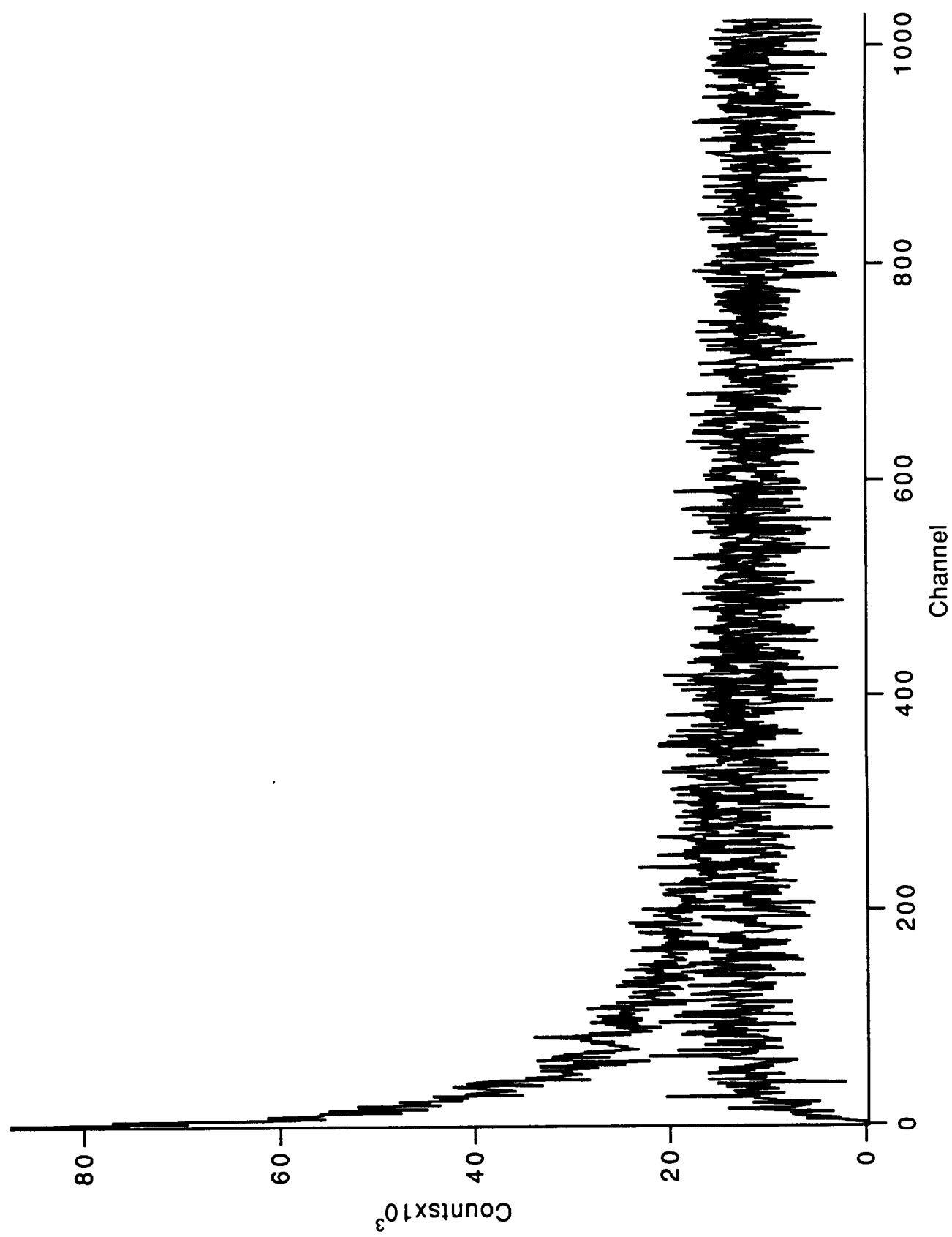


Figure 12b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of Cl<sub>2</sub>O<sub>2</sub>.

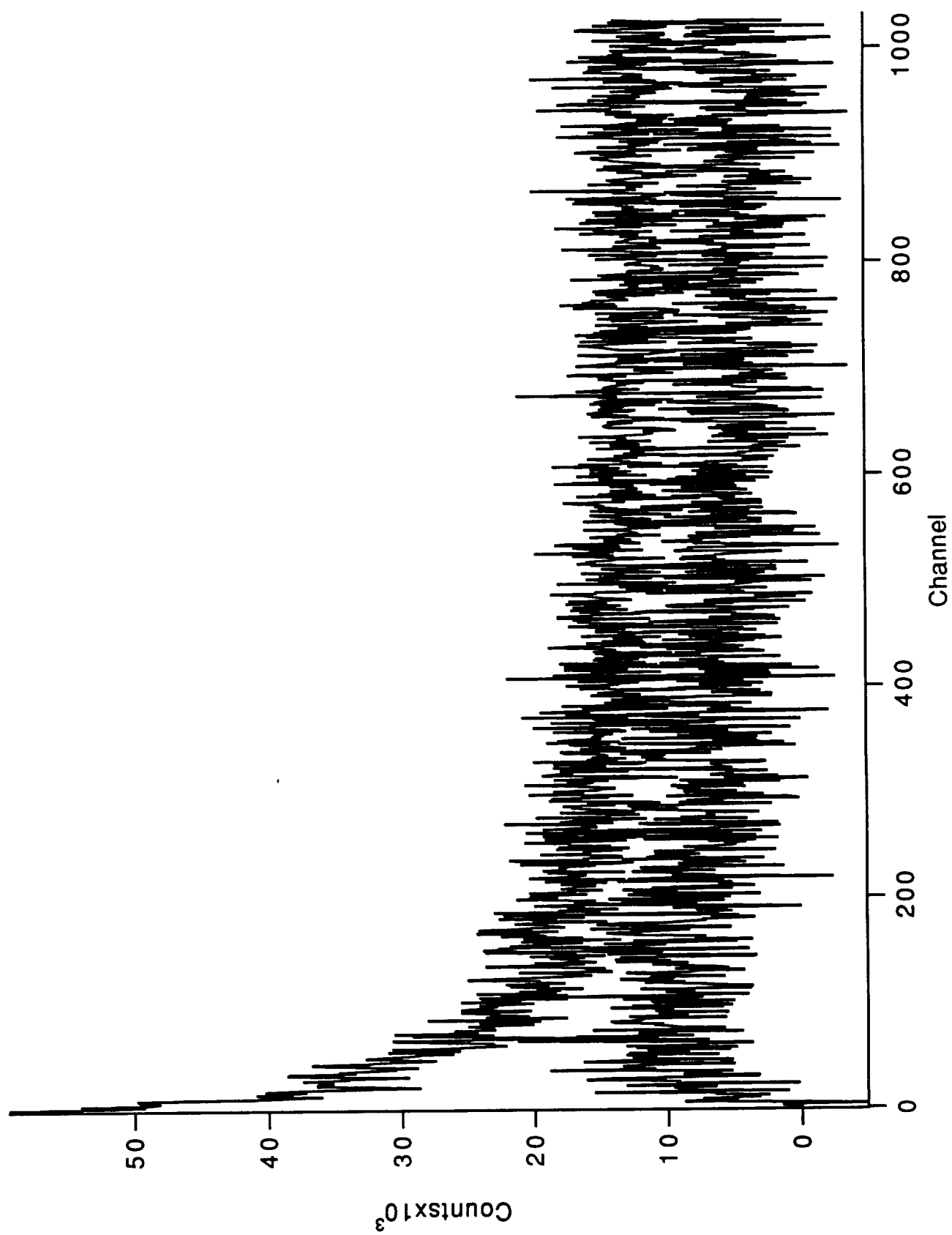


Figure 13b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of Cl<sub>2</sub>O<sub>2</sub>.

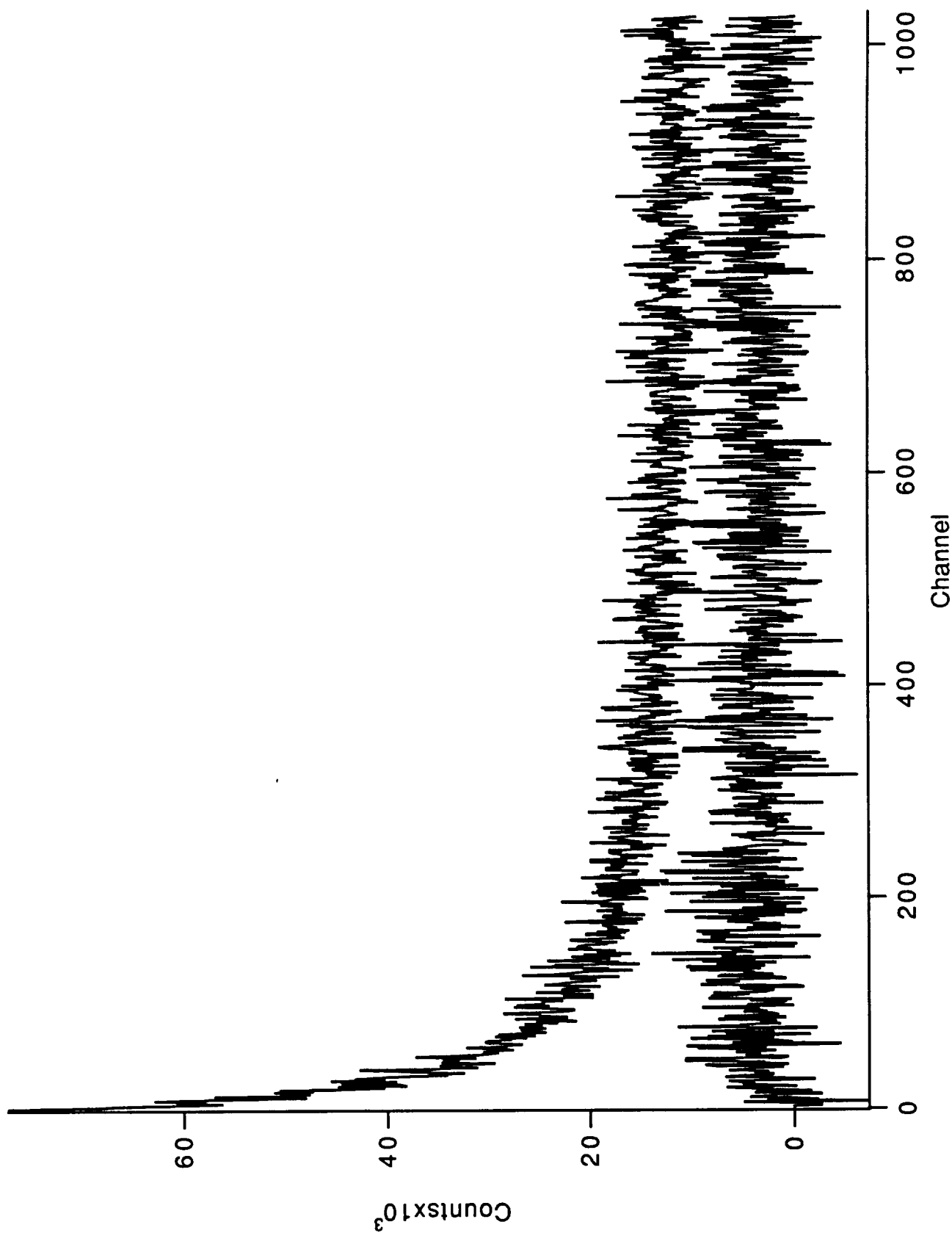


Figure 14b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of  $\text{Cl}_2\text{O}_2$ .

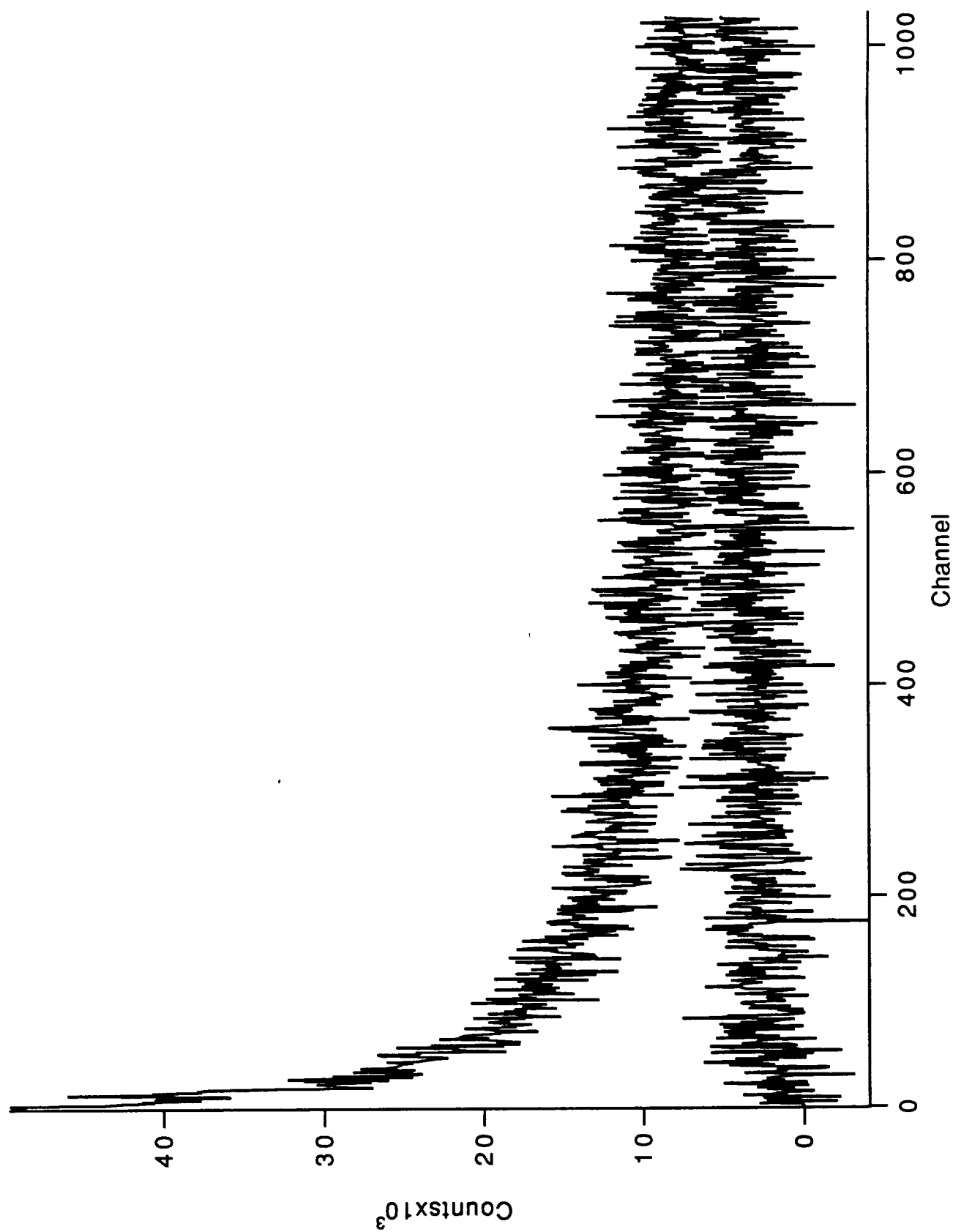


Figure 15b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of Cl<sub>2</sub>O<sub>2</sub>.

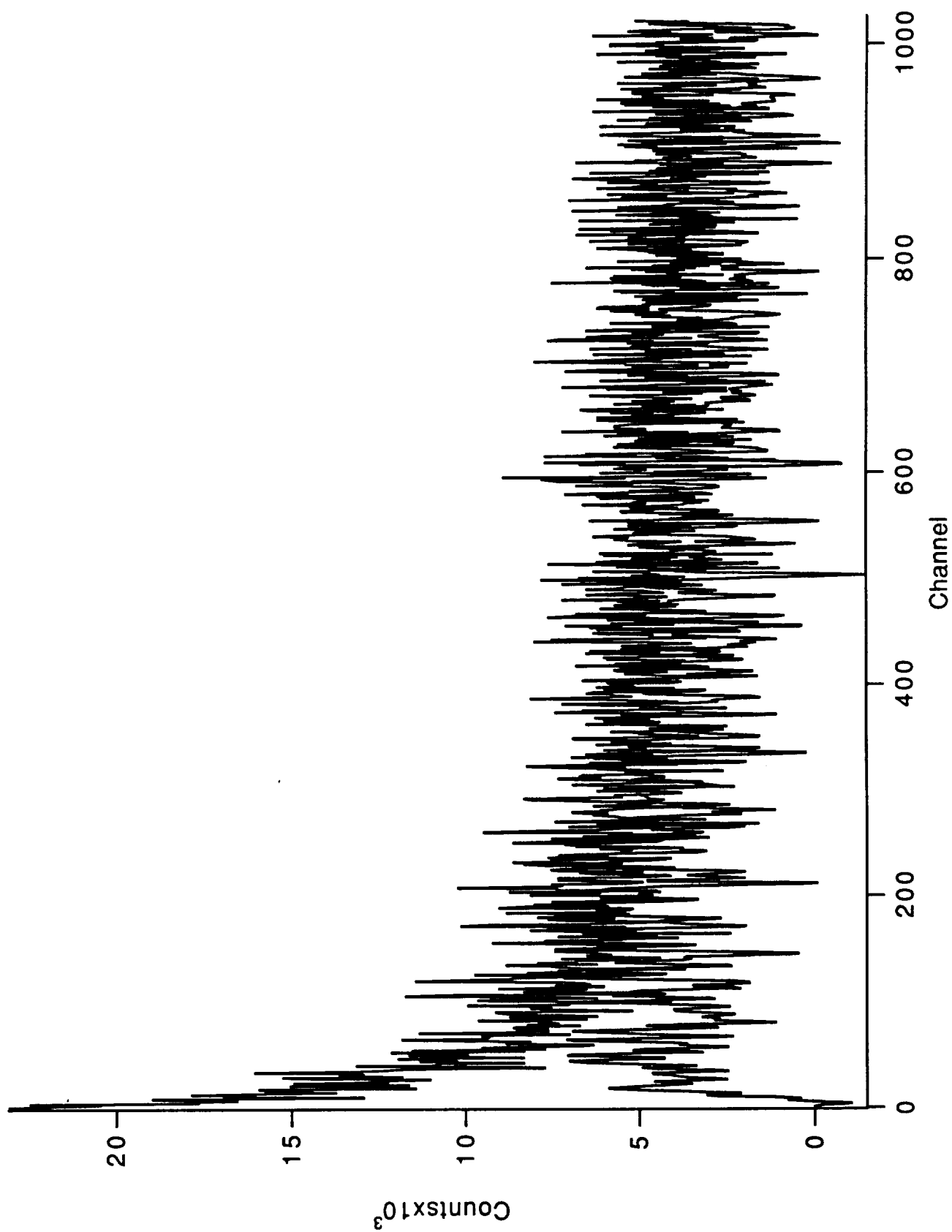
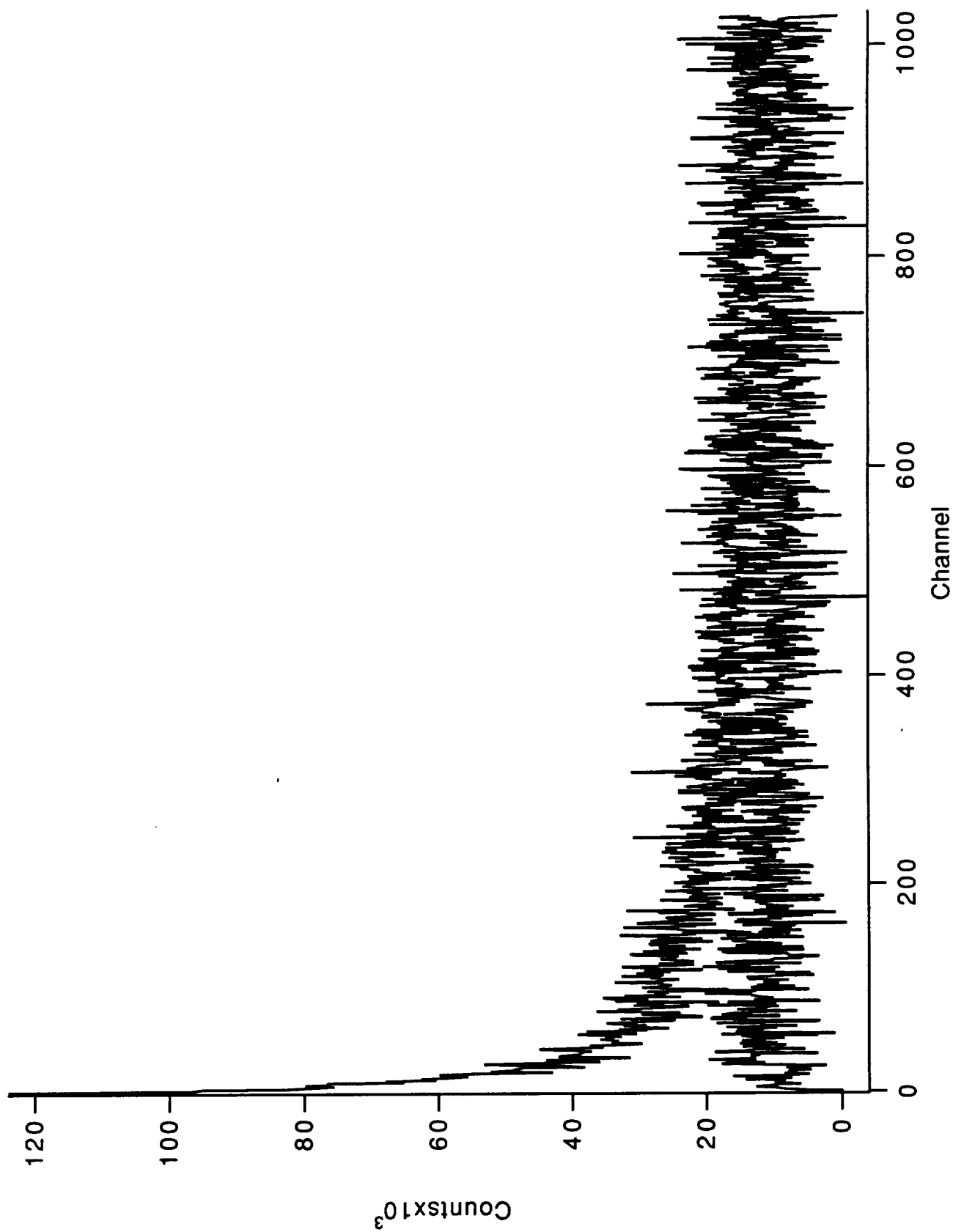


Figure 16b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of  $\text{Cl}_2\text{O}_2^-$ .



**Figure 17b. Multichannel analyzer output for 51+. Bottom curve is the contribution to 51+ from the fragment ion of  $\text{Cl}_2\text{O}_2$ .**

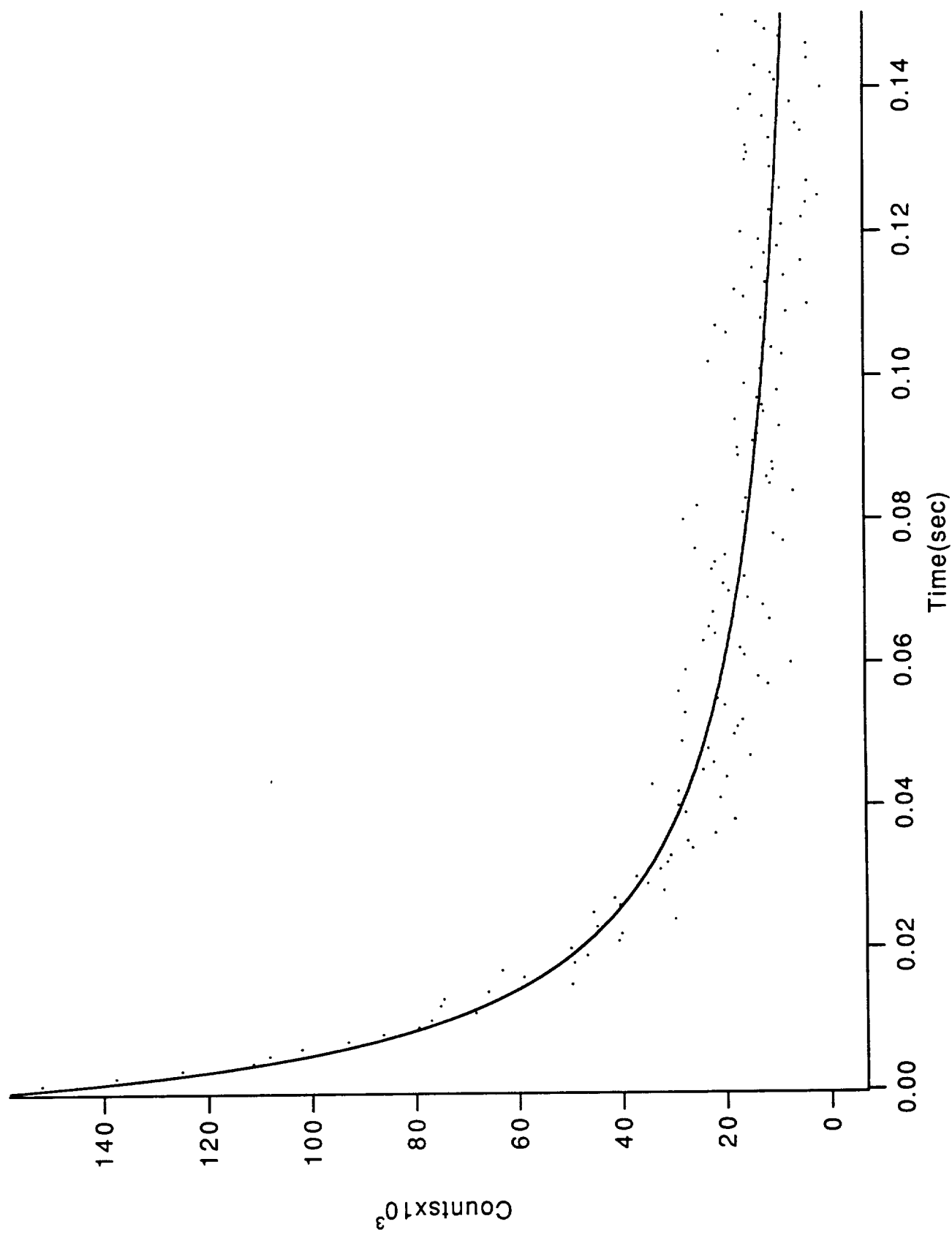
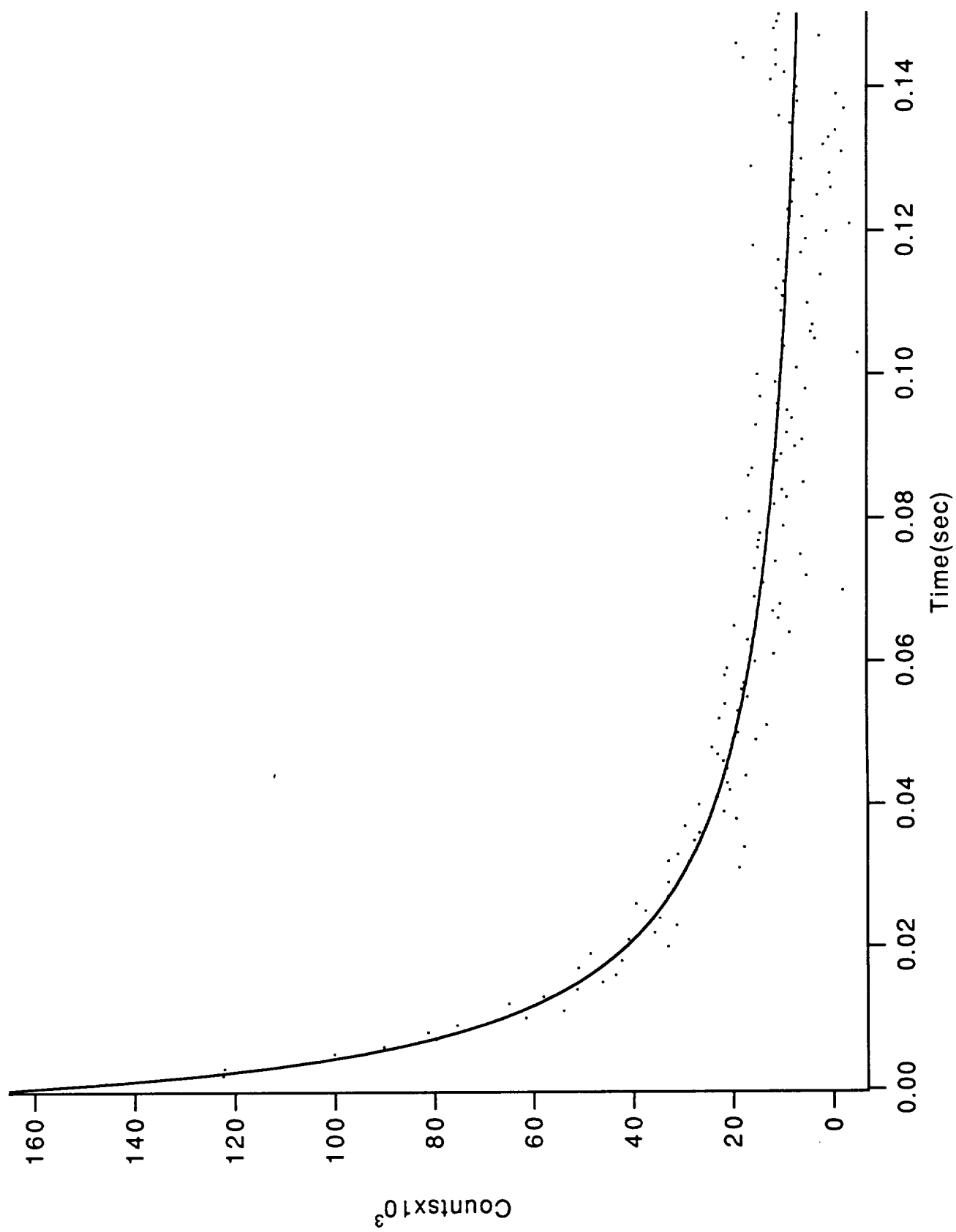
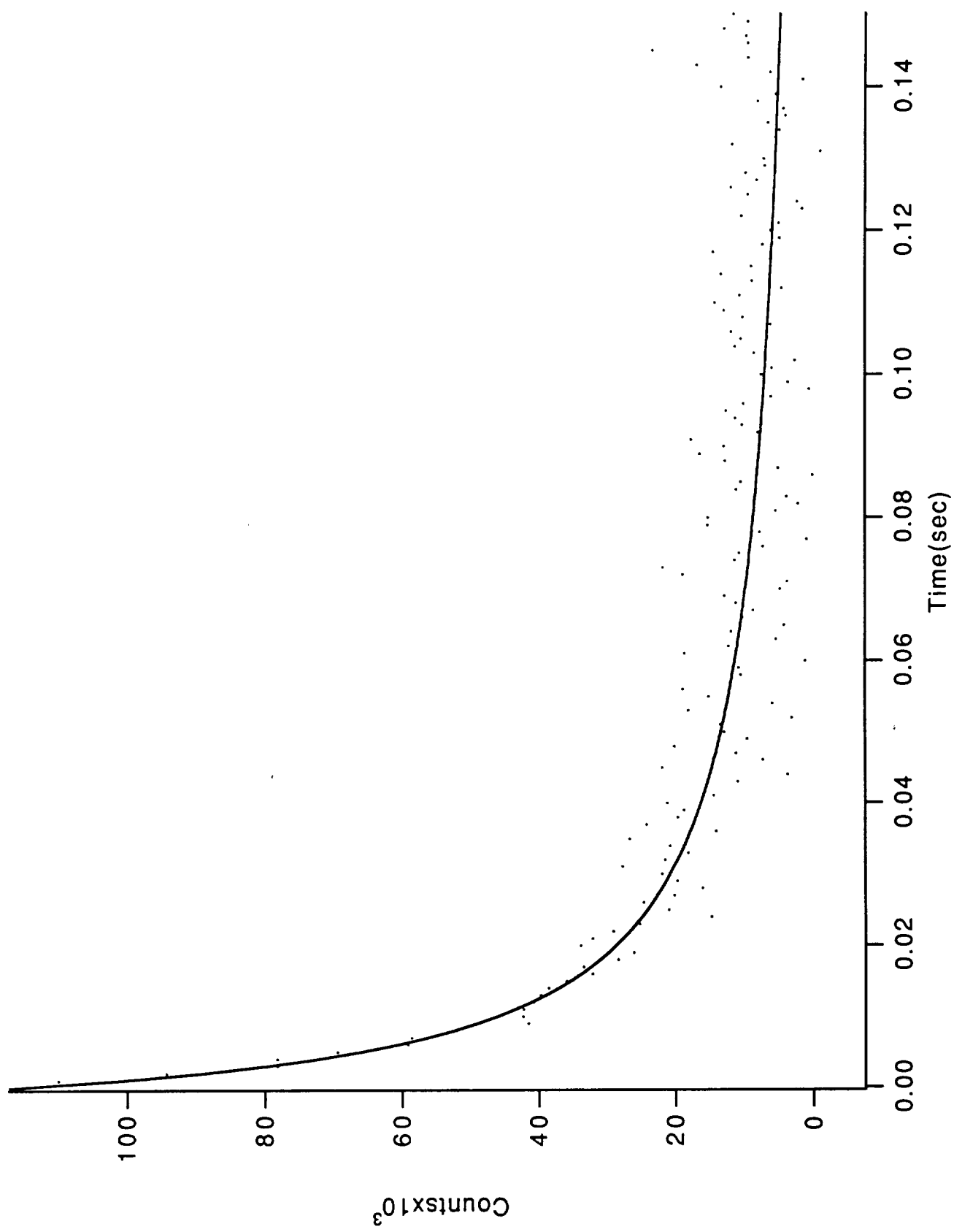


Figure 7c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.

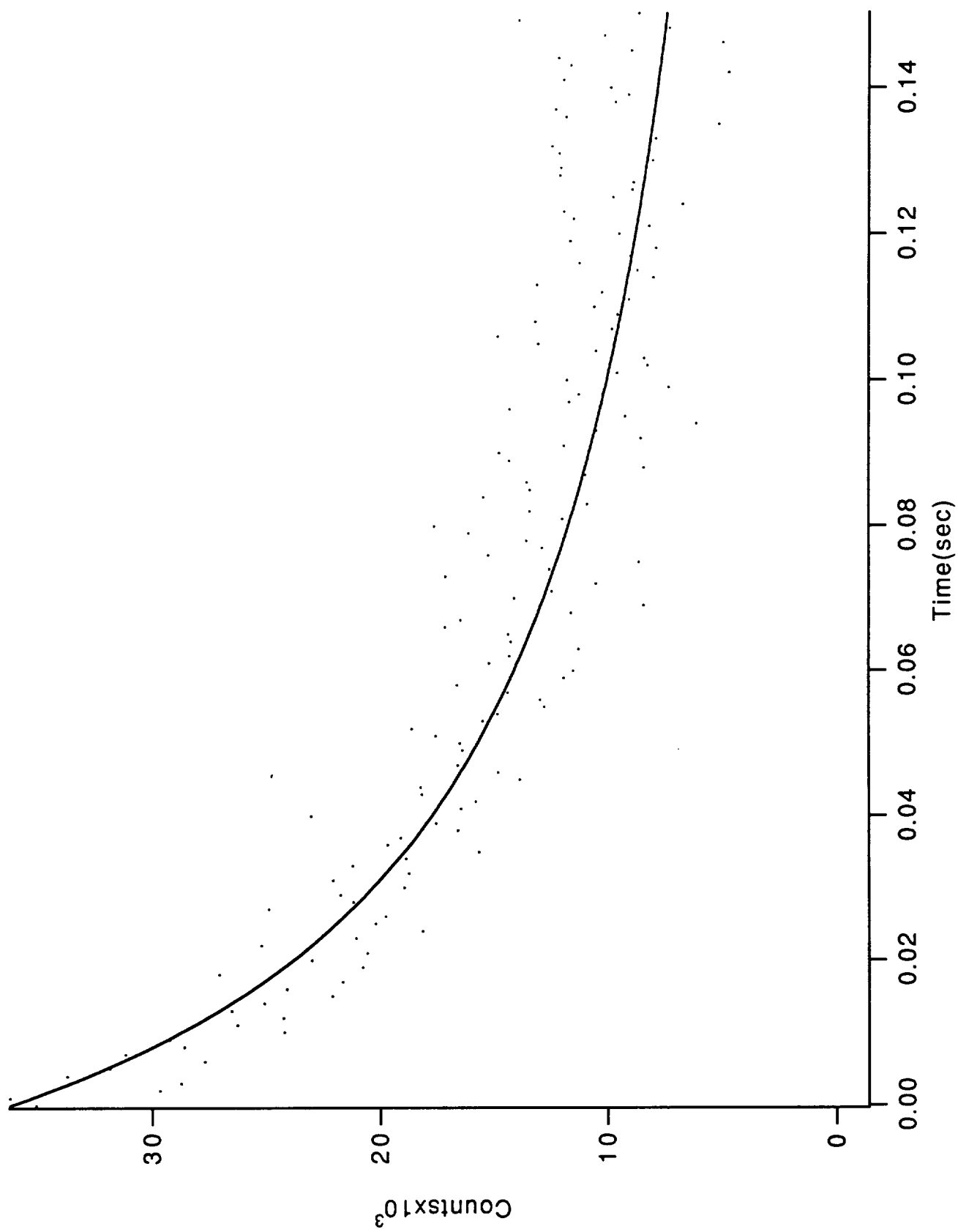


**Figure 8c.** Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.





**Figure 9c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.**



**Figure 10c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.**

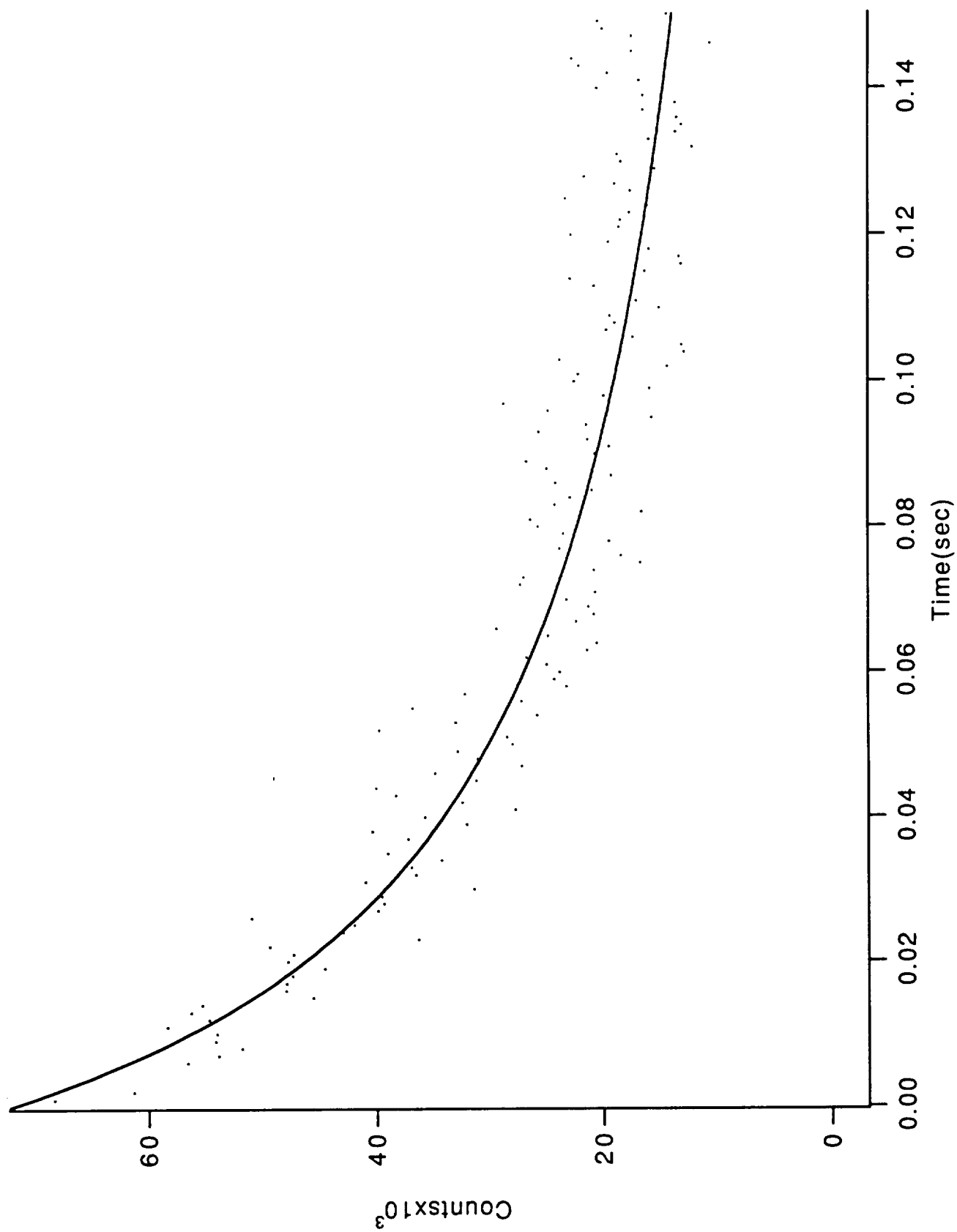


Figure 11c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.

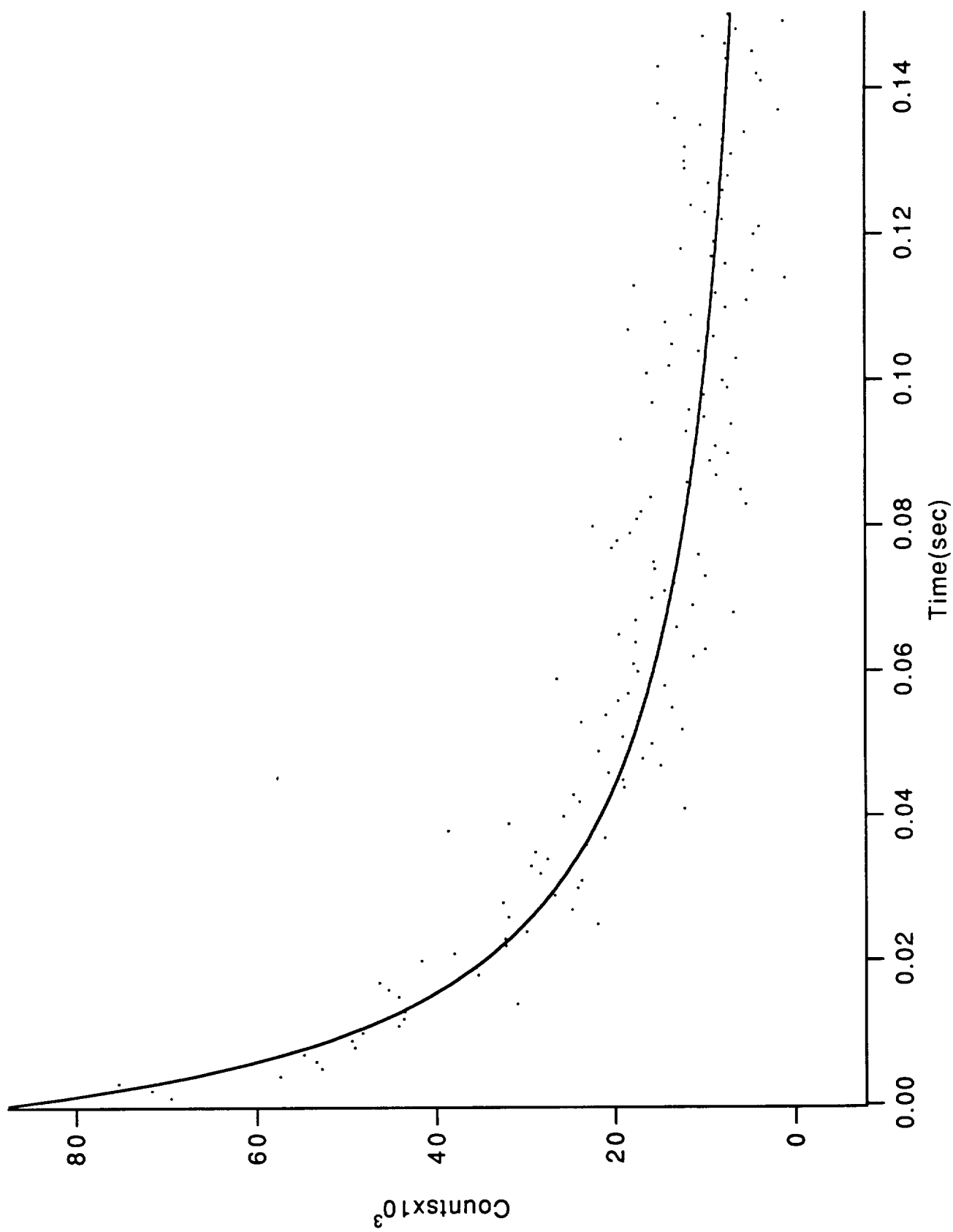


Figure 12c. Plot of  $\text{ClO}^+$  versus time after the laser pulse. Solid line is the second order kinetic fit to the data.

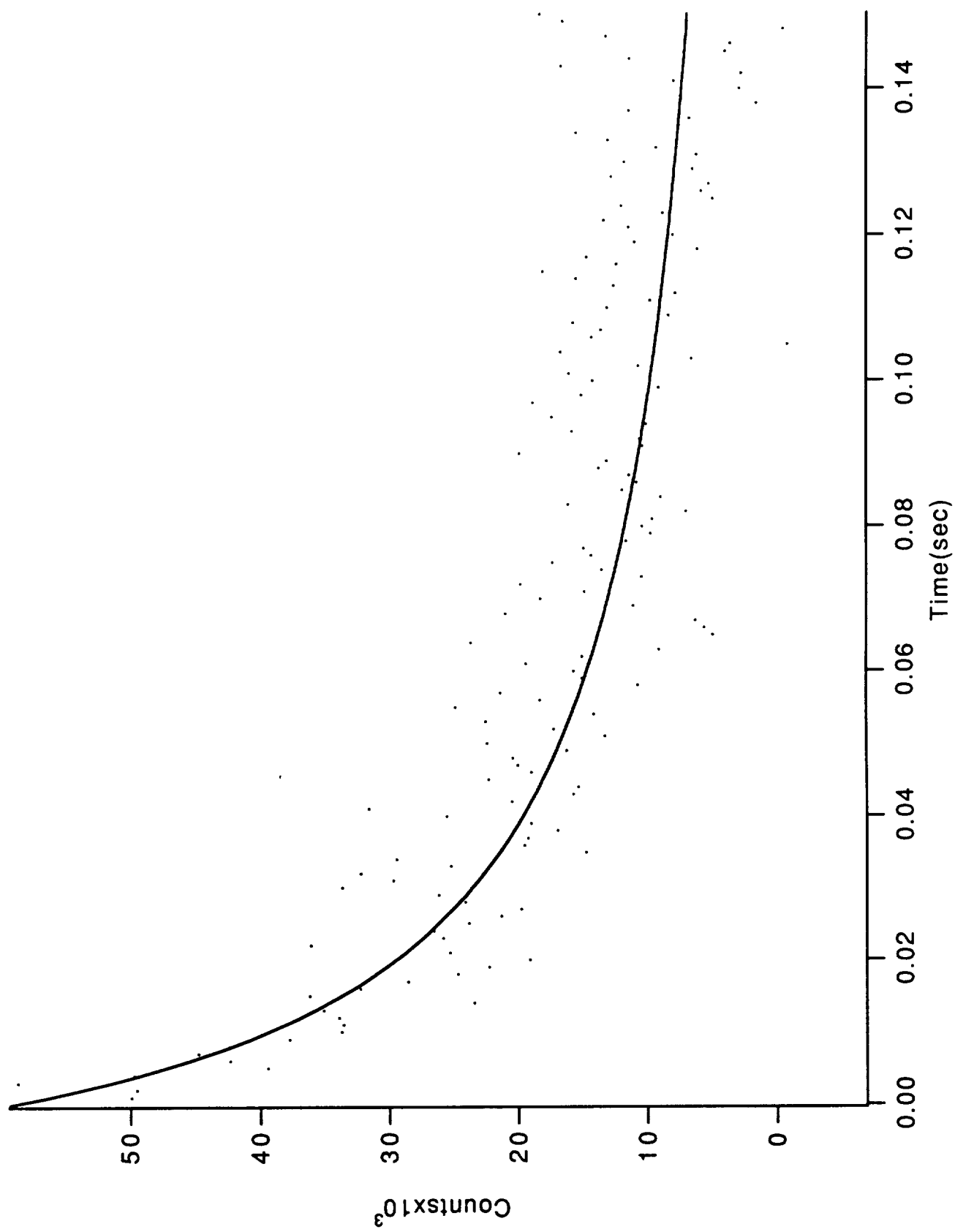
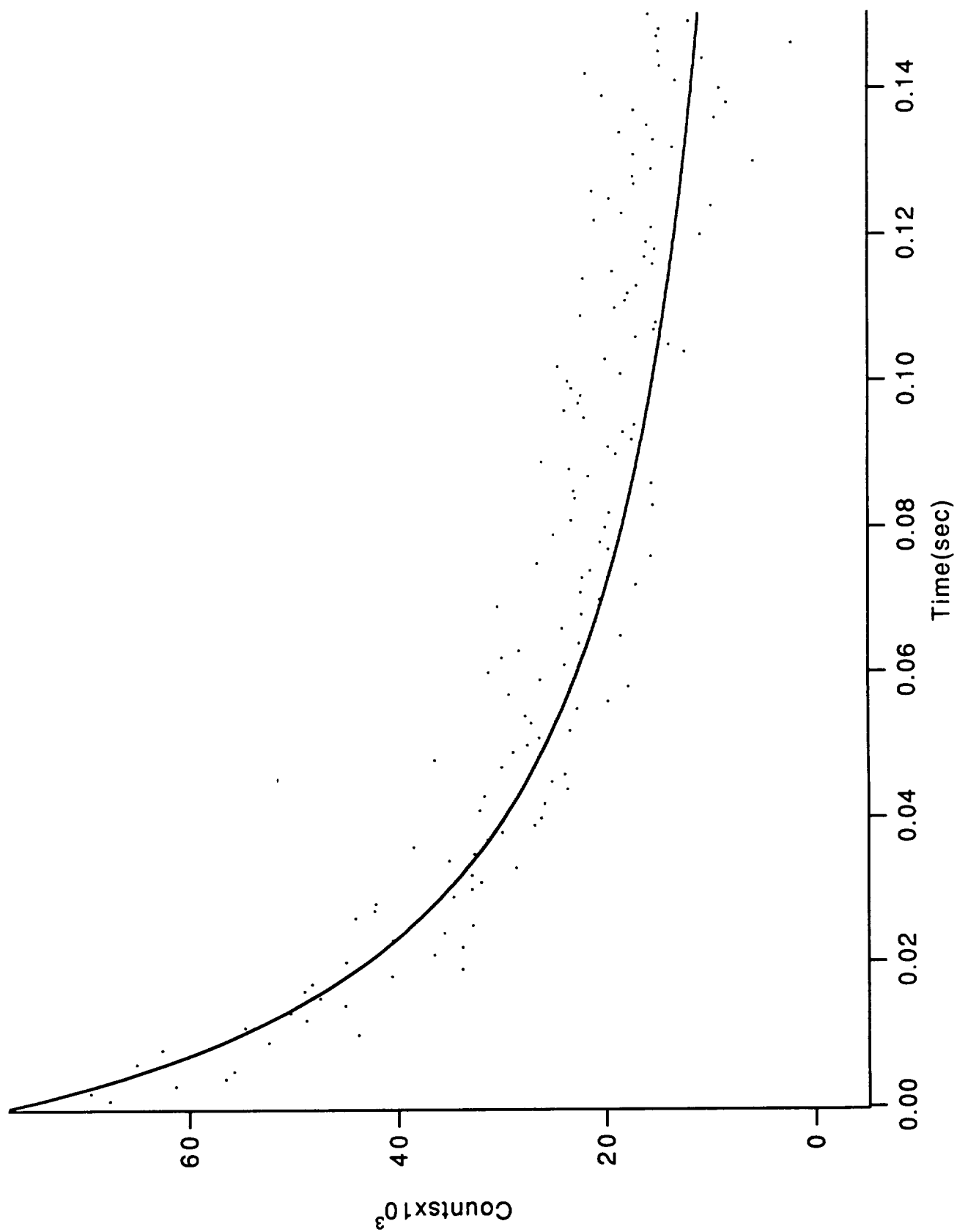


Figure 13c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.



**Figure 14c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.**

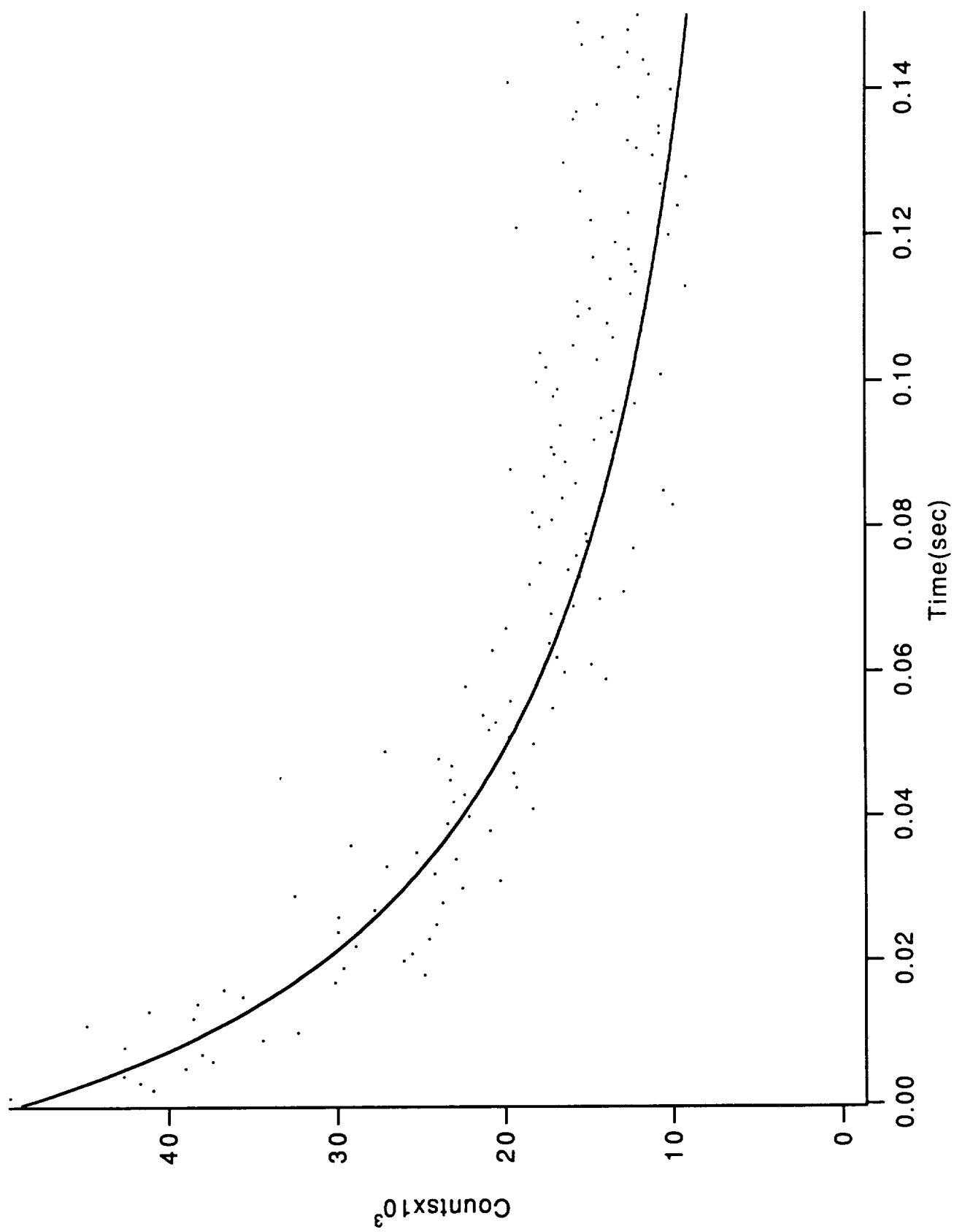


Figure 15c. Plot of  $\text{ClO}^+$  versus time after the laser pulse. Solid line is the second order kinetic fit to the data.

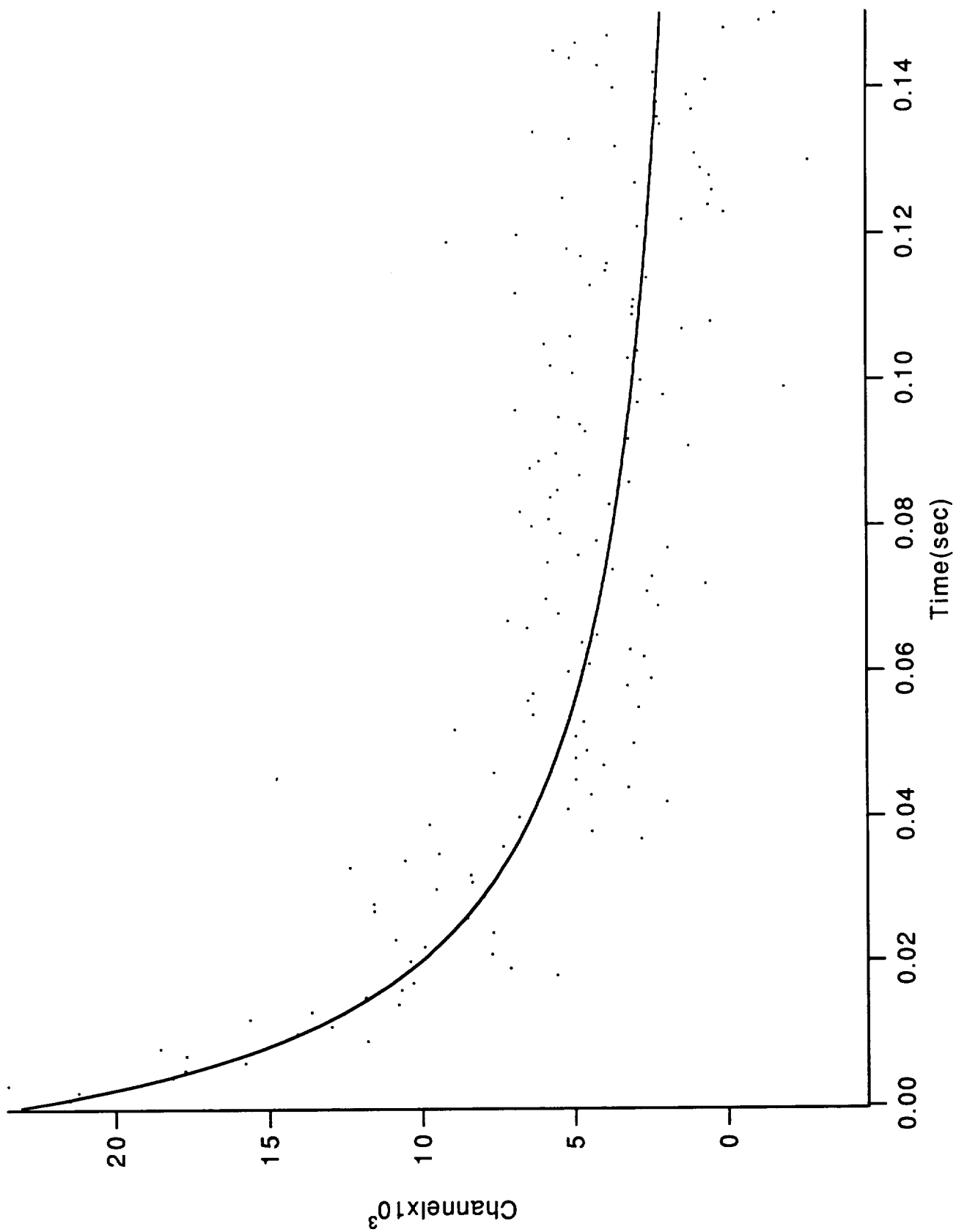


Figure 16c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.



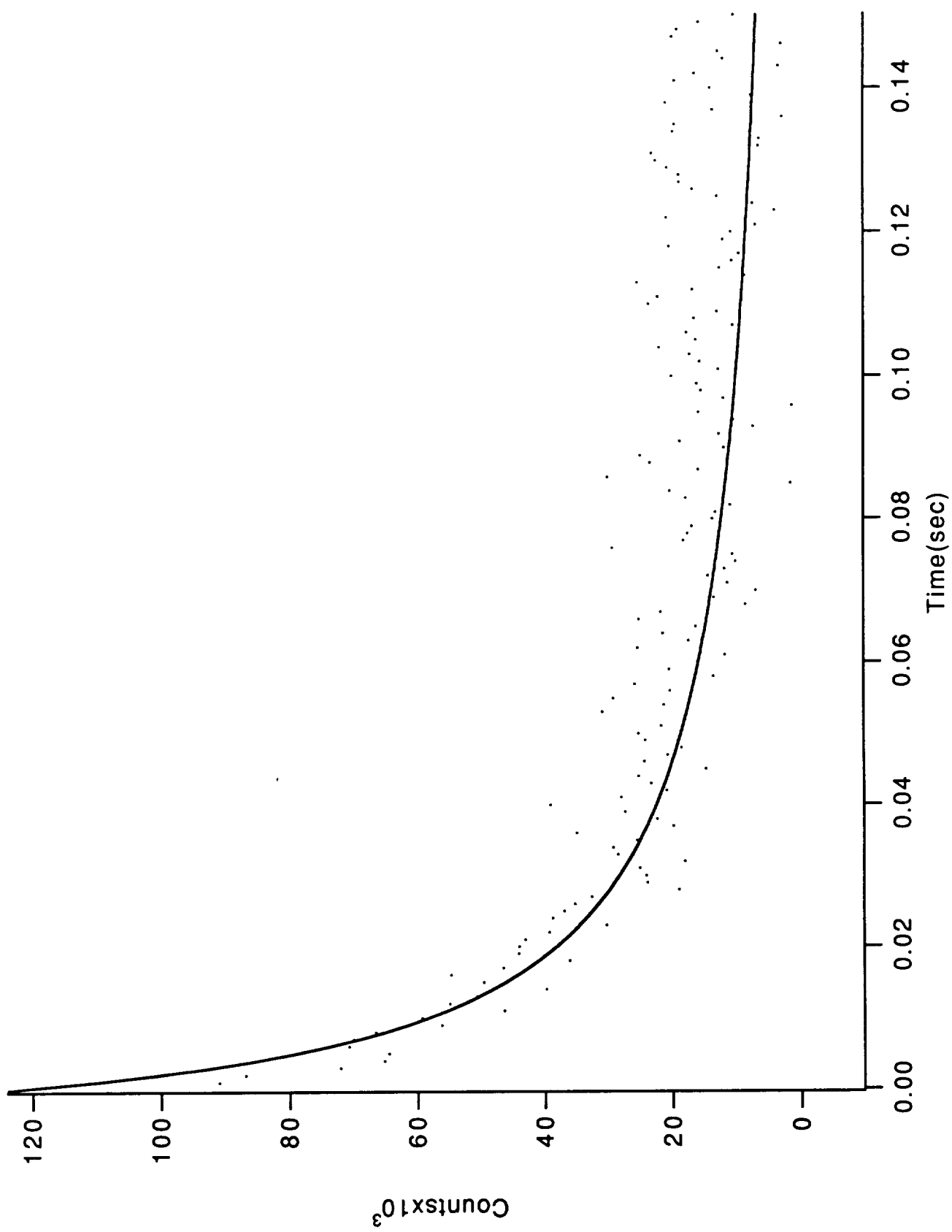


Figure 17c. Plot of ClO<sup>+</sup> versus time after the laser pulse. Solid line is the second order kinetic fit to the data.

One additional small downward correction is applied to the ion signals for some residual dimer that is not pumped from the cell between laser pulses. This is evident from a small positive signal observed at  $102^+$  at time zero. This small signal is simply subtracted from the data.

## Data Reduction

The rate constants for the self reaction of ClO were determined from the measured plots of the decay of ClO radicals. Second order kinetic behavior was expected, and so the time dependence of ClO was fit to the following relationship

$$2kt = [\text{ClO}]_t^{-1} - [\text{ClO}]_0^{-1} \quad (7)$$

where  $k$  is the rate constant,  $[\text{ClO}]_0$  is the initial concentration, and  $[\text{ClO}]_t$  is the concentration after time  $t$ . The data were fit with the above expression by an iterative nonlinear least squares computer fit with the times used restricted to the first third of the experiment in order to improve the accuracy of the data. The ClO data, and the computer generated curves, are shown in Figures 7c through 17c.

The resulting kinetic parameters determined from the decay of ClO were used to calculate a curve for the time dependence of ClO dimer. These curves were plotted along with the data for  $\text{Cl}_2\text{O}_2^+$  in Figures 7d through 17d. In each case the curve was scaled to superimpose the  $\text{Cl}_2\text{O}_2^+$  data. As can be seen, the shapes of the curves match very well, indicating that this is the dominant reaction channel for the decay of ClO under these conditions.

Because the self-reaction of ClO is a second order process, the absolute concentrations of ClO must be known to calculate the rate constants. In order to determine these concentrations from the mass spectrometric intensities, the response factor for ClO relative to that for  $\text{O}_2$  was measured using ionizing energies and other instrumental parameters identical to those employed in the rate measurements. The ClO was generated by mixing an excess of Cl atoms, which were generated by passing a room temperature mixture of  $\text{Cl}_2$  and Ar through a microwave discharge, with an  $\text{O}_3$ - $\text{O}_2$  mixture. The reaction products, which consisted of an  $\text{O}_3$ -free mixture of  $\text{Cl}_2$ ,  $\text{O}_2$ , Ar, and ClO, were introduced into a flow reactor, the ClO "titrated" with an excess of NO, and MBMS was used to measure the intensity of the  $\text{NO}_2$  peak relative to that from the known partial pressure of  $\text{O}_2$ . The response factor for  $\text{NO}_2$  relative to that for  $\text{O}_2$ , which was determined using a standard gas mixture, was used to calculate the absolute concentrations of  $\text{NO}_2$ .

The response factor for ClO was used to calculate rate constants from the data given in Figures 7c through 17c. The resulting rate constants are summarized in Table 3. These rate constants are within the range of those previously obtained at these temperatures.<sup>13</sup>

## PHOTOLYSIS OF ClO DIMER

The photolysis cross section and products produced by the photolysis of ClO dimer are key elements in the proposed mechanism for chlorine regeneration. Recent theoretical work has shown that the dimer should have the proxy structure. Consequently, photolytic decomposition will either produce ClO, resulting in the termination of the reaction chain, or Cl atoms, which will continue the chain reaction. In the chemical systems used in this study it would not be possible to distinguish between these reaction paths because the Cl atoms will react with O<sub>2</sub> to form ClO in a few microseconds, depending on the temperature and pressure. This time is near the limits of the time resolution of the MBMS system used for this study. Consequently, no attempt was made to identify and measure the photolysis products in the flow reactor. However, it should be noted that this experiment may be feasible using an alternative MBMS system available at MRI. The transfer of the experimental apparatus to the alternative system was not possible in the time available.

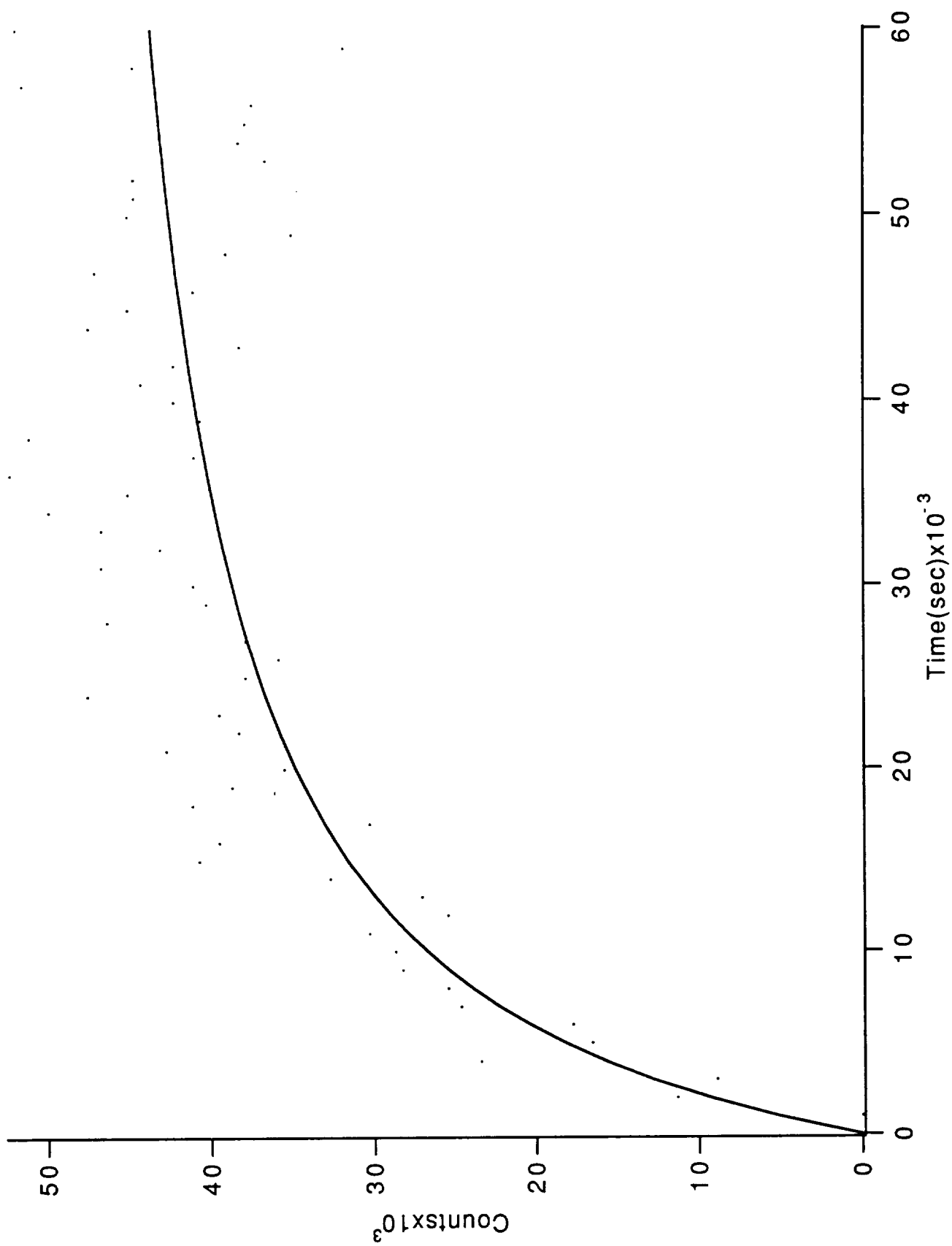
Considering the problems in making the photolysis measurements in the flow reactor, the alternative experiment in which the ClO dimer was photolyzed in the molecular beam was selected. This experiment, which was included in the original proposal, eliminates the recombination or reaction of the photolysis products. However, there is very strong possibility that the transnational "recoil" energies may be as much as several electron volts, with the angular distribution of the recoil velocity vectors largely anisotropic.<sup>17</sup> Consequently, if the photolysis occurs in a well-collimated molecular beam, a majority of the products will probably be directed out of the beam and, depending on the experimental geometry and the angular resolution of the detector, may be lost.

In order to circumvent the recoil energy problem, the experimental configurations shown in Figure 18 was selected. In this arrangement the laser beam is crossed with the molecular beam and the electron beam in the center of the ion source of the quadrupole mass spectrometer. This provides a maximum residence time for the photolysis products in the ionizing region, and consequently maximum sensitivity. The only major disadvantage is that of simultaneous multiphoton ionization (MPI), which may produce fragment ions which must be distinguished from photolysis products. Since MPI is second order with photon density, and photolysis is essentially linear, it is possible to determine the existence of a problem by reducing laser power and should generally be possible to make a satisfactory correction.

**Table 3. SUMMARY OF MEASURED RATE CONSTANTS**

| Temperature<br>(°C) | Pressure<br>(torr) | Initial ClO<br>concentration<br>(molecules/cc x10 <sup>12</sup> ) | Rate constant<br>(cc/molecule sec x10 <sup>-13</sup> ) |
|---------------------|--------------------|---|--|
| -20                 | 75                 | 133   | 1.49 <sup>a</sup>                                      |
| -40                 | 30                 | 67  | 2.14 <sup>a</sup>                                      |
| -40                 | 78                 | 226   | 2.51   |
| -40                 | 77                 | 260   | 2.86   |
| -40                 | 78                 | 144   | 2.64 <sup>a</sup>                                      |
| -40                 | 120                | 300   | 1.87 <sup>a</sup>                                      |
| -56                 | 78                 | 118   | 2.13 <sup>a</sup>                                      |
| -63                 | 30                 | 7.8   | 4.30   |
| -65                 | 32                 | 47  | 2.94   |
| -66                 | 32                 | 43  | 3.00   |
| -67                 | 75                 | 206   | 3.74   |
| -70                 | 78                 | 64  | 5.02 <sup>a</sup>                                      |
| -66                 | 117                | 65  | 7.46   |

<sup>a</sup> Non-simultaneous measurements.



**Figure 7d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.**

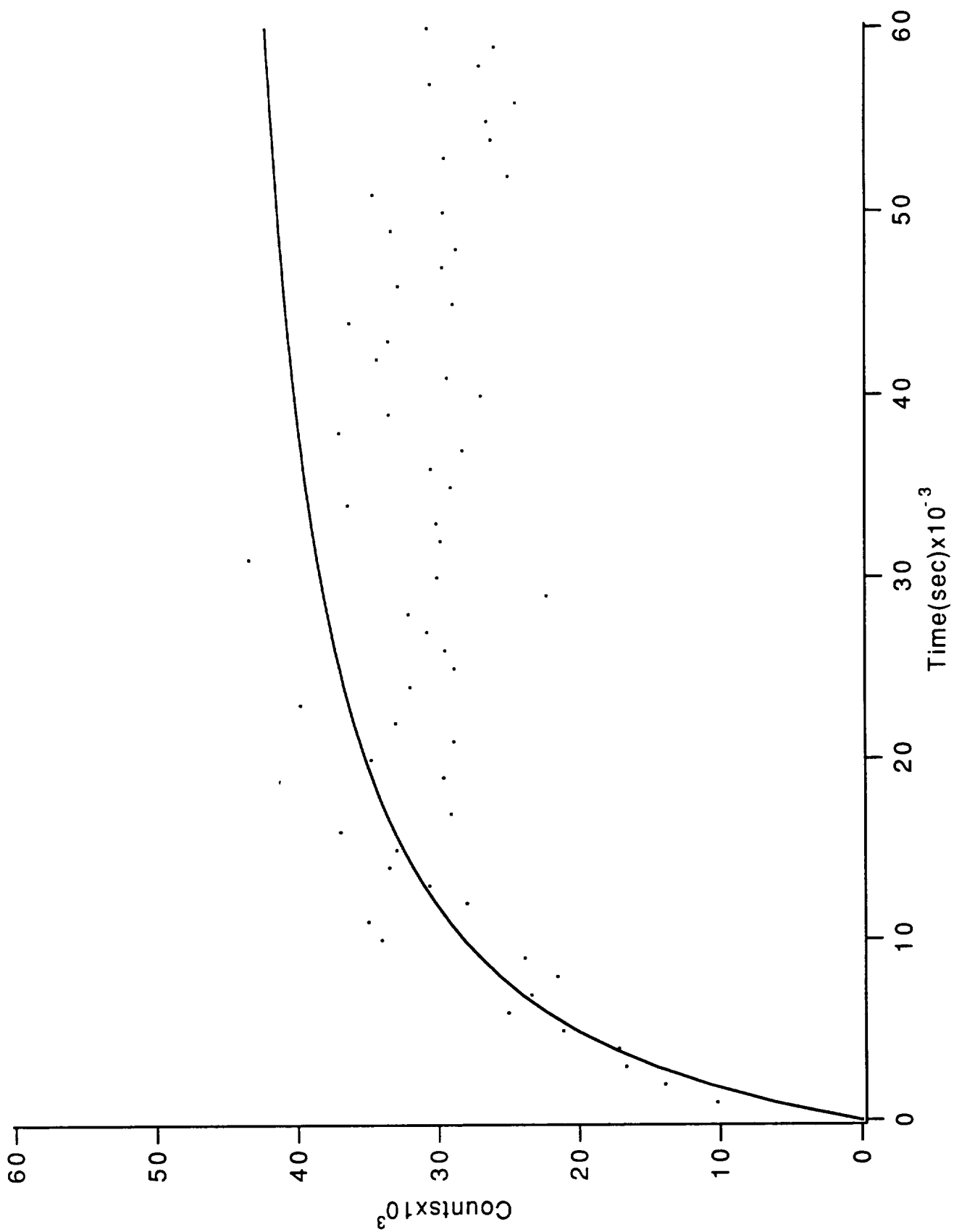


Figure 8d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

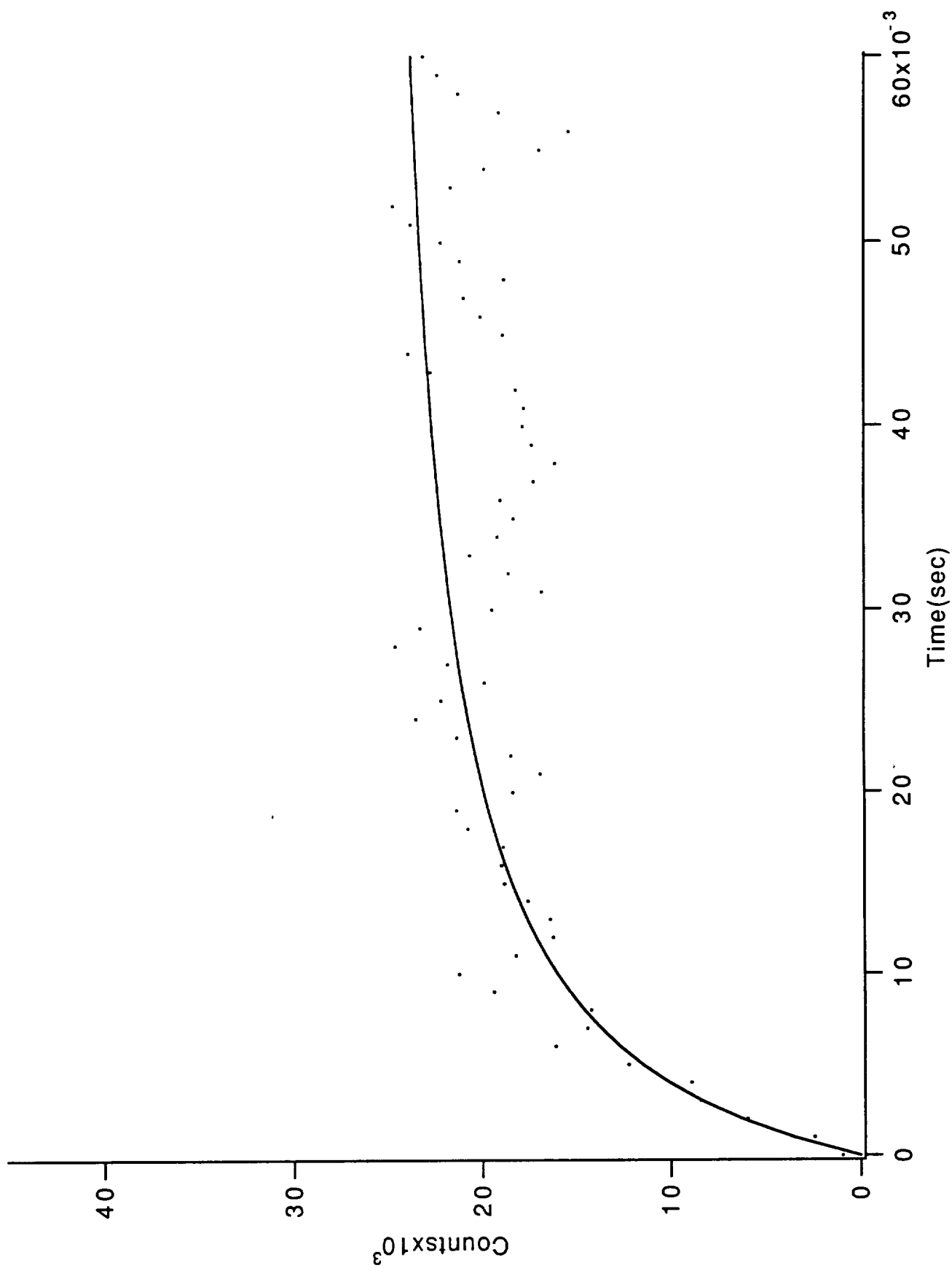
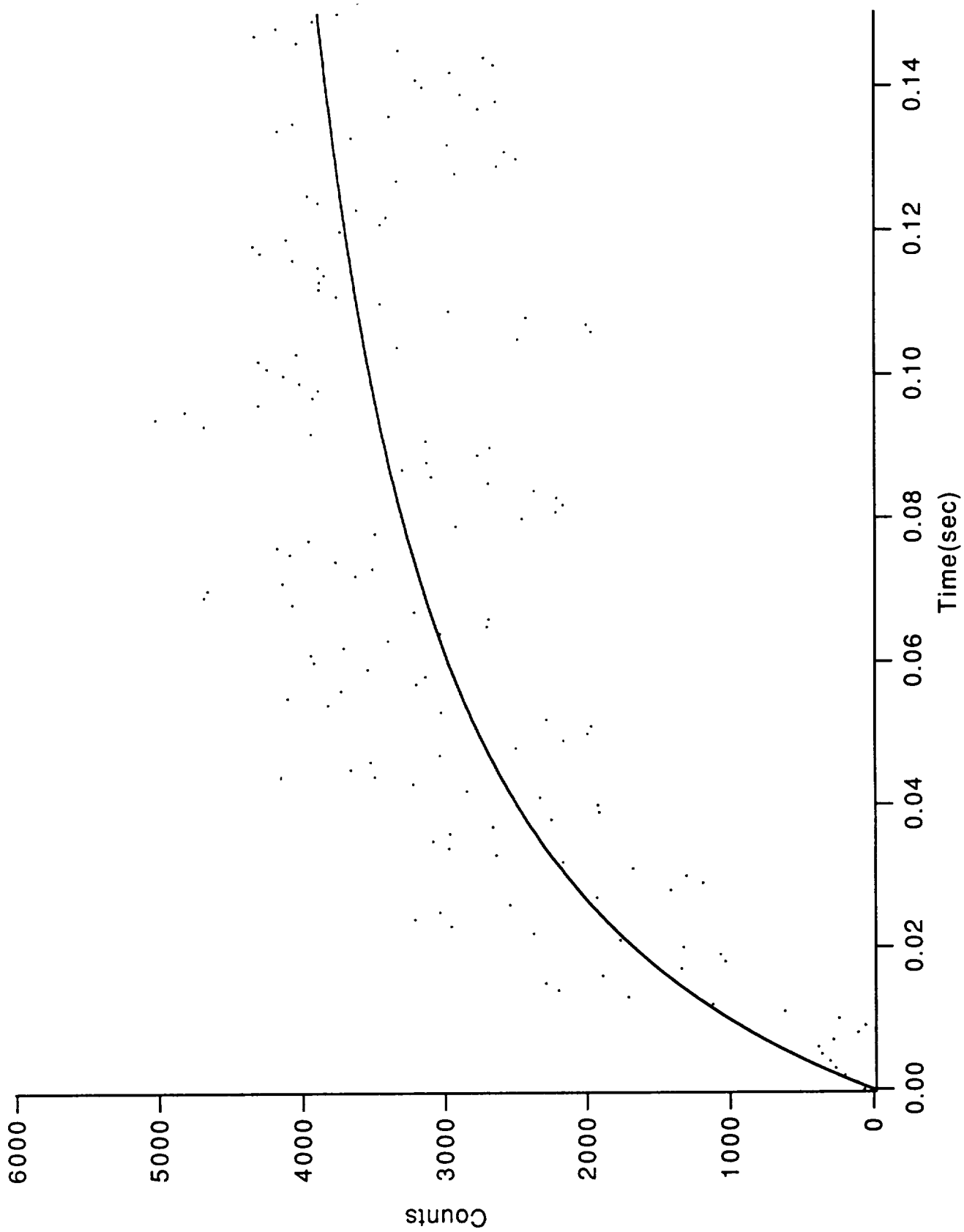


Figure 9d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.



**Figure 10d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.**



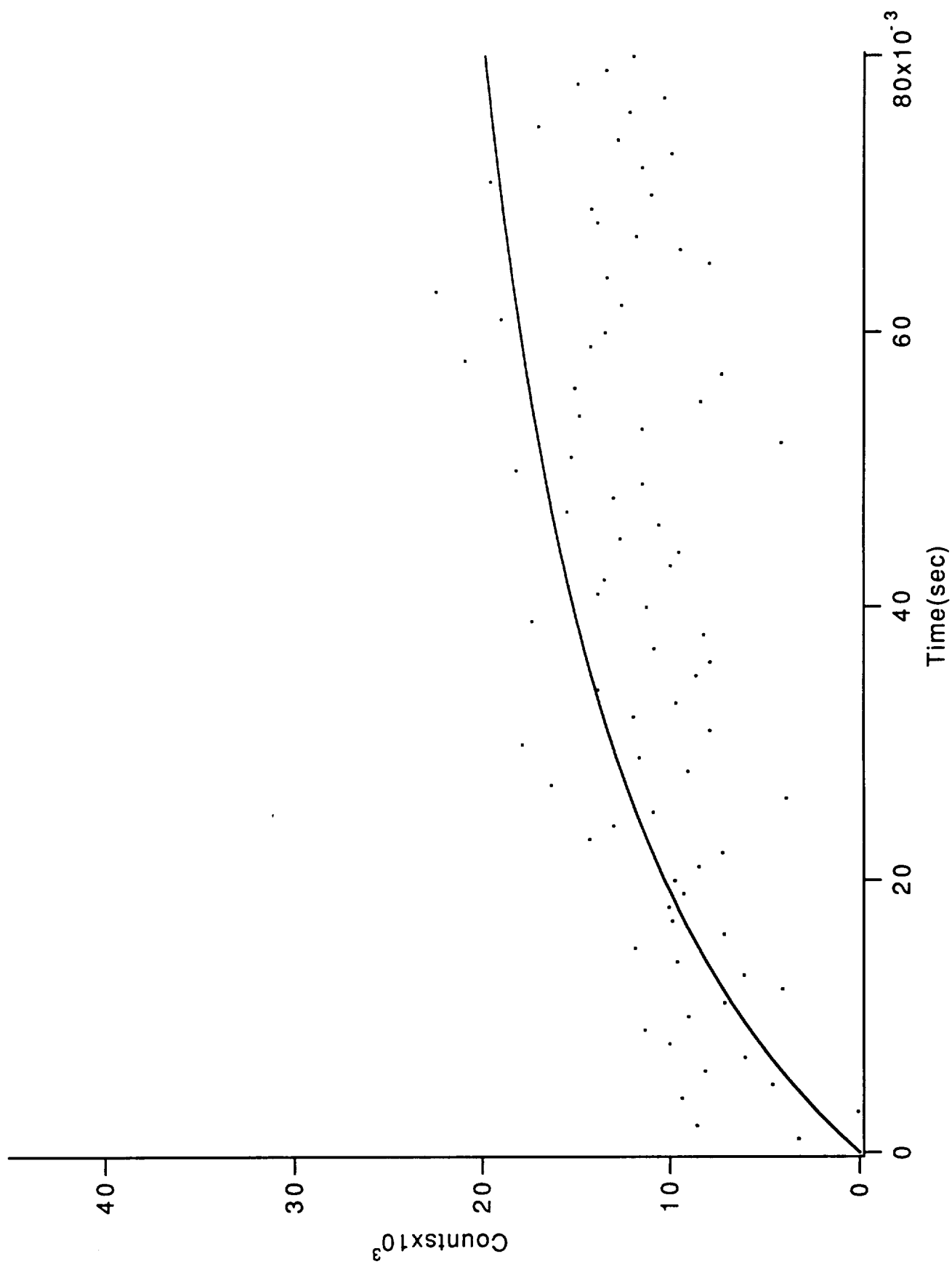


Figure 11d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

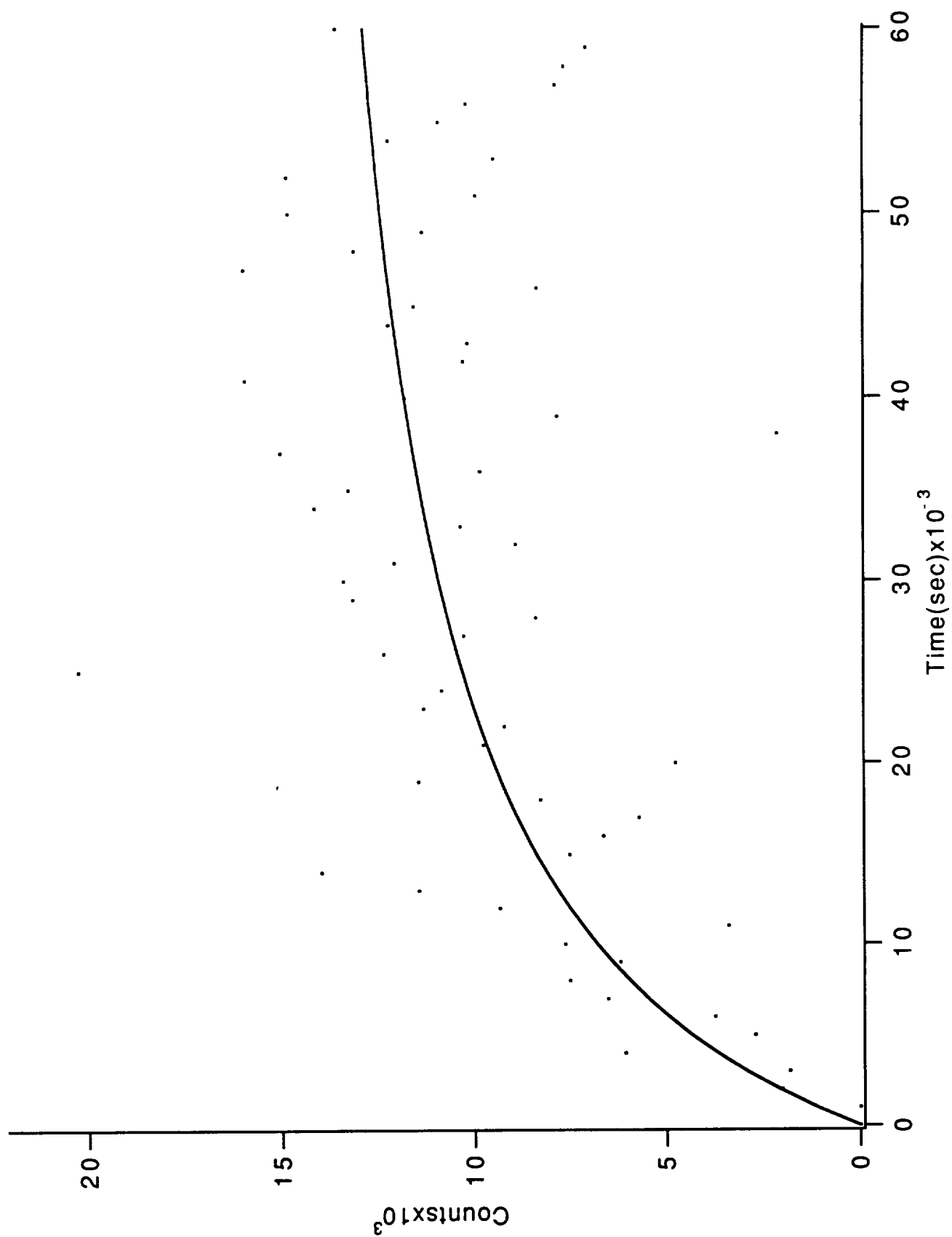


Figure 12d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

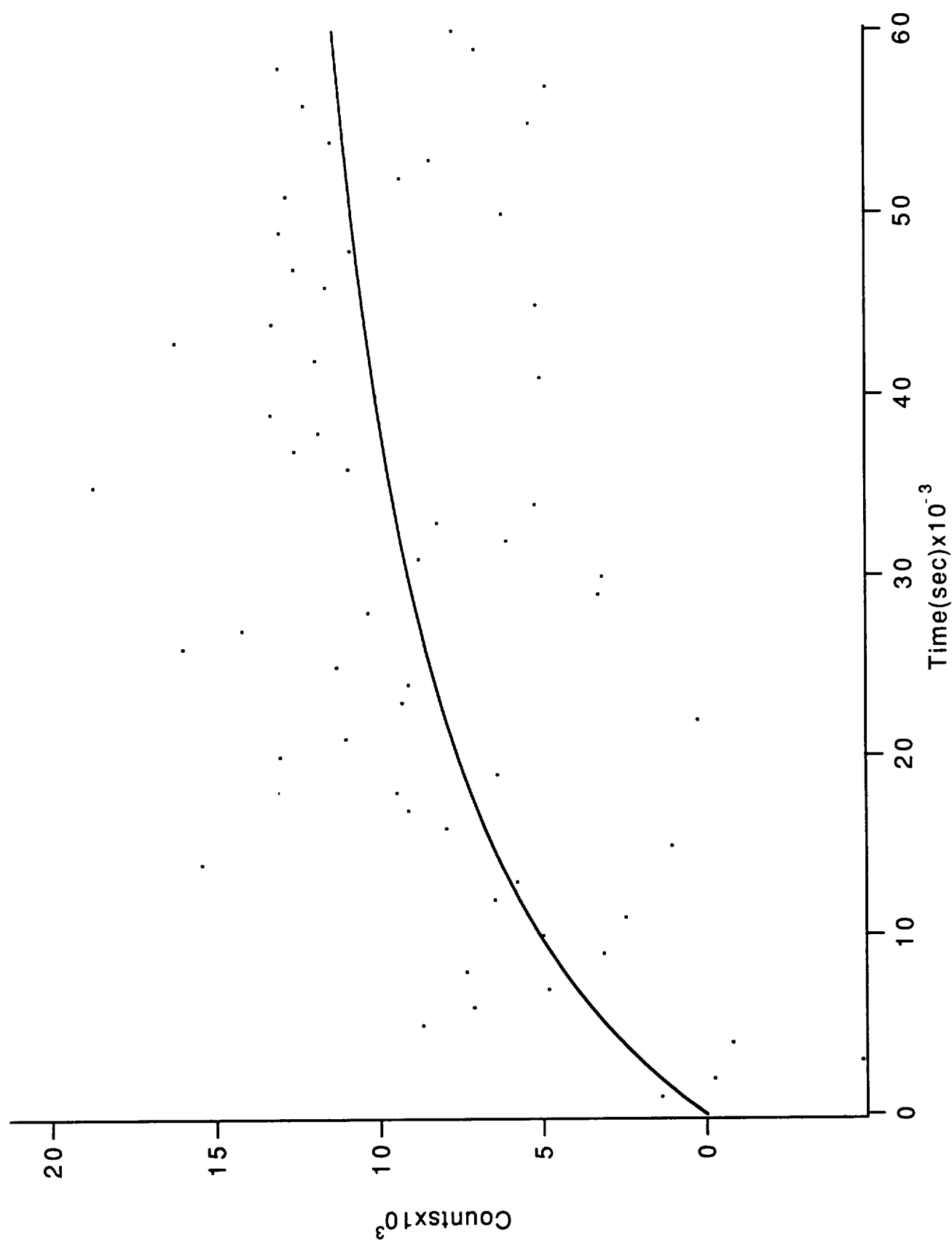


Figure 13d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

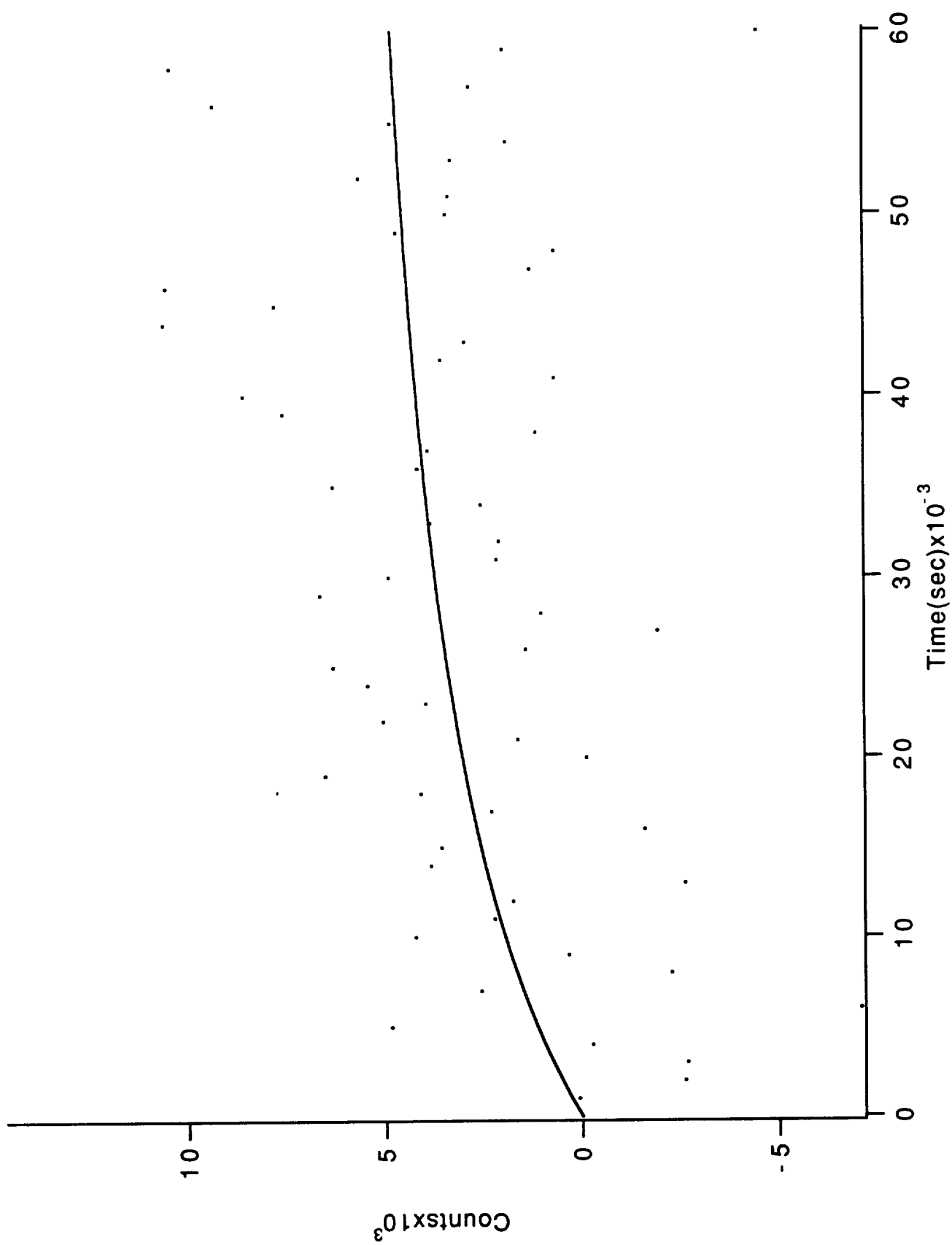


Figure 14d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

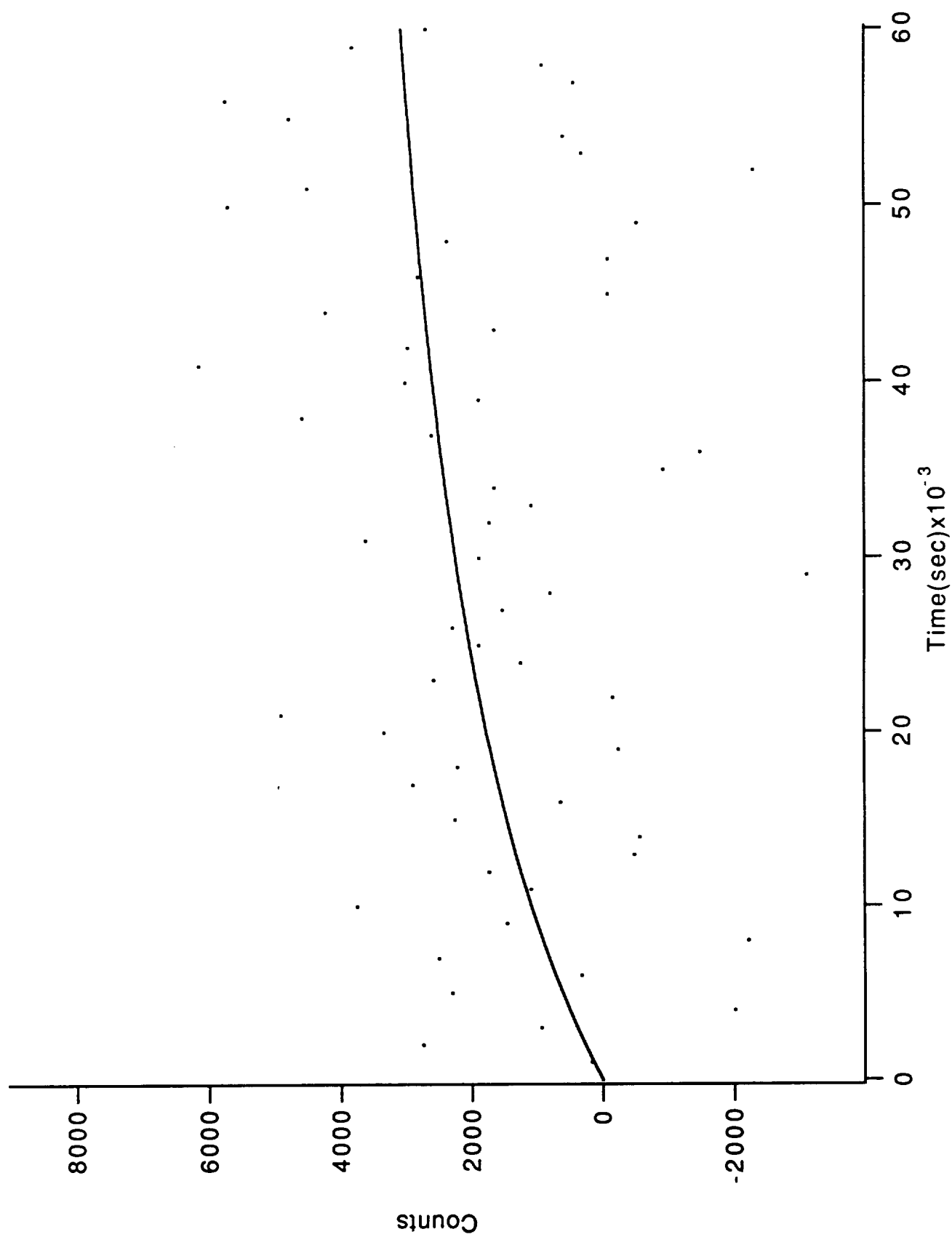


Figure 15d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

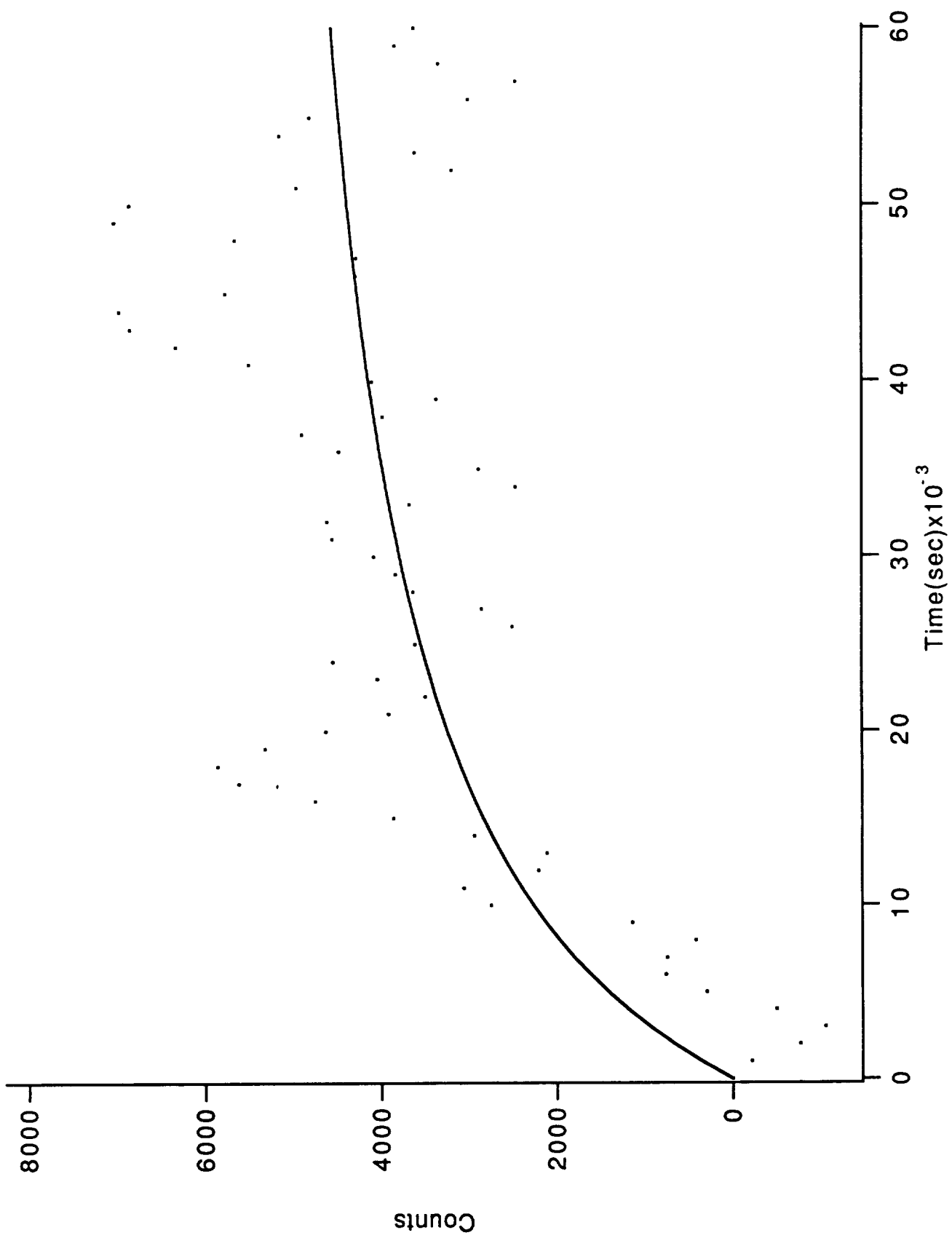


Figure 16d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.

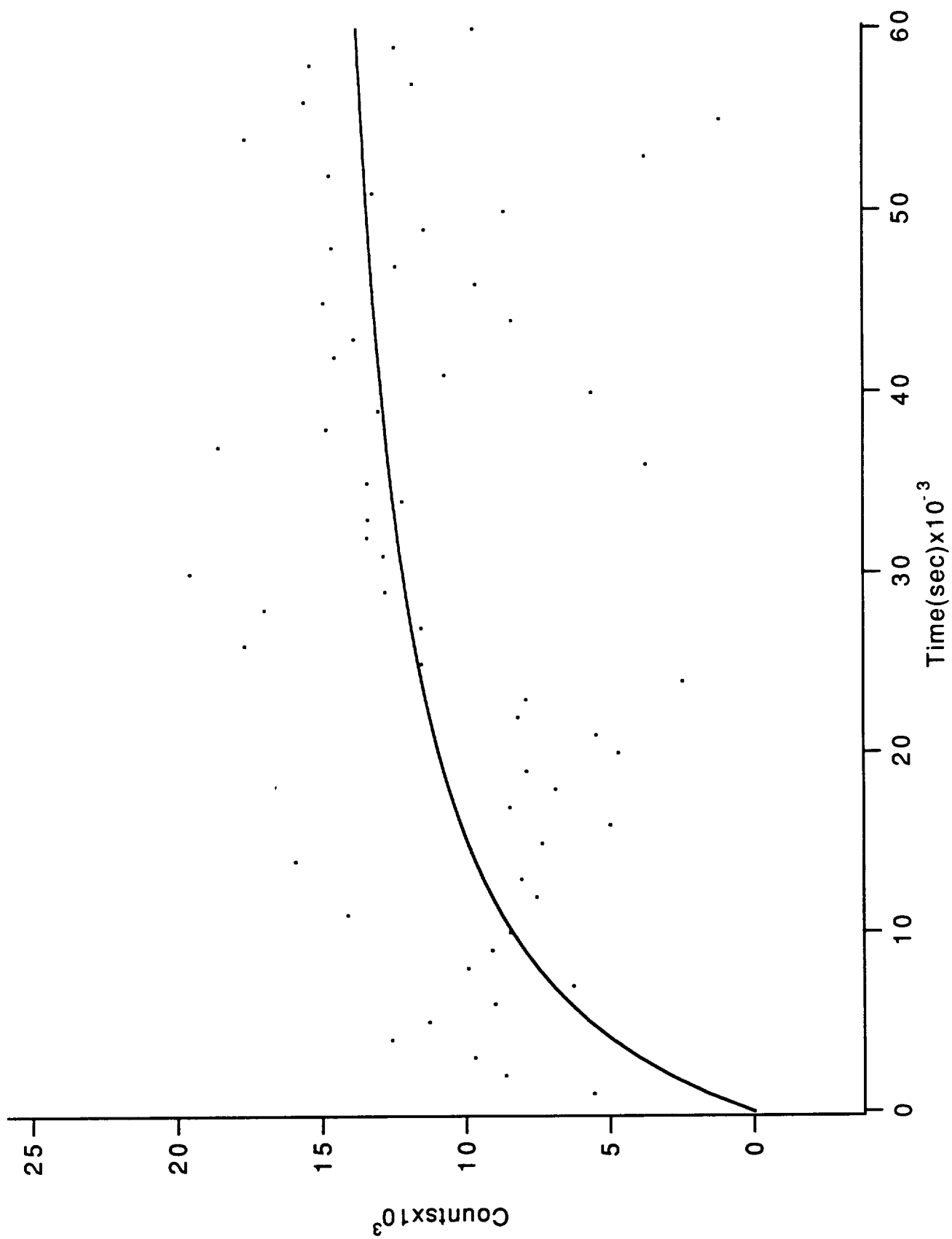
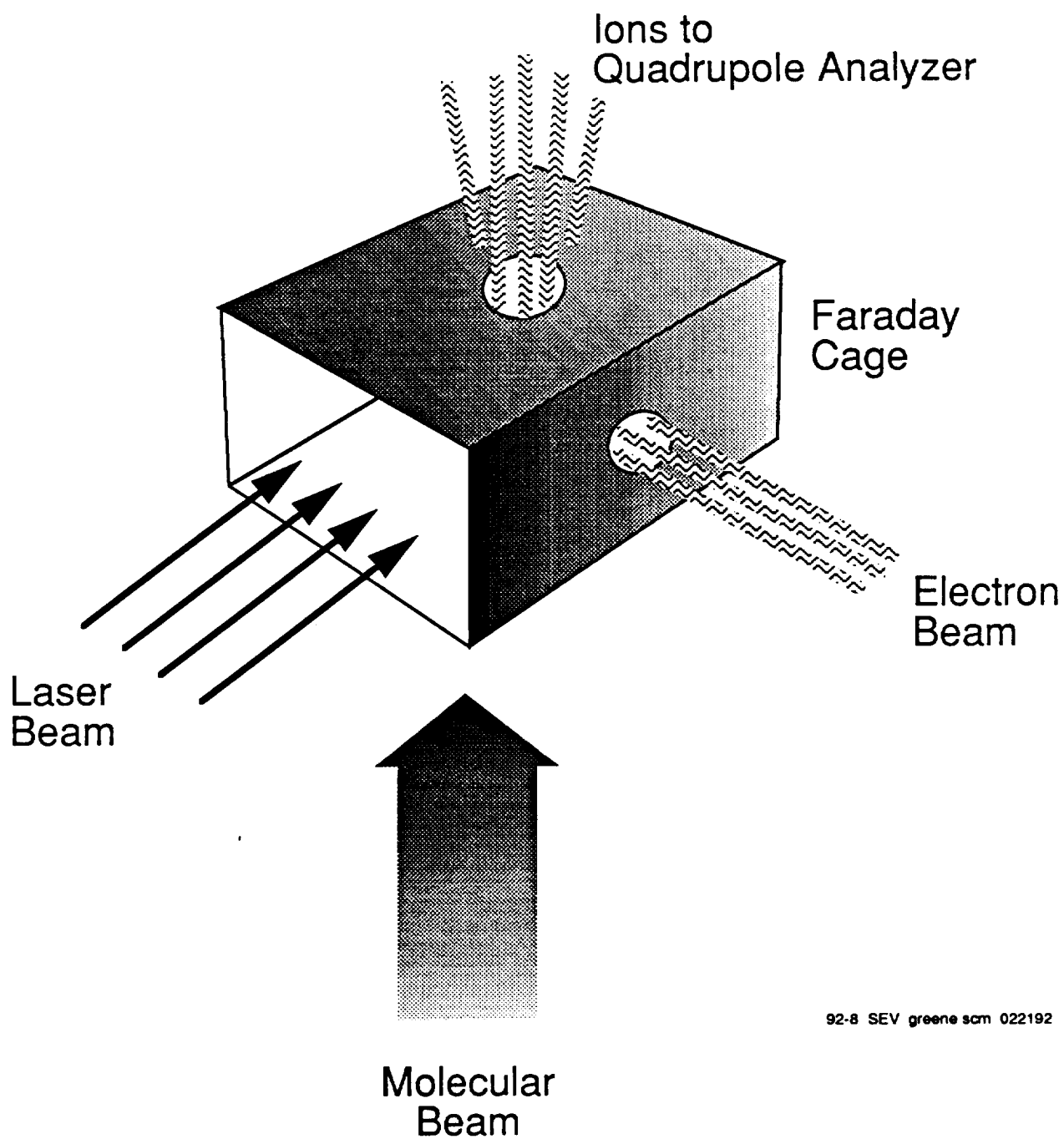


Figure 17d. Plot of  $\text{Cl}_2\text{O}_2^+$  as a function of time after the laser pulse. Solid line is the kinetic fit to the data.



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**Figure 18. Apparatus for the laser photolysis of chlorine oxides.**



This experiment shown in Figure 18 was set up, with the quadrupole located in its normal position as shown in Figure 1. The 266 nm 4th harmonic beam from the Molectron MY 34 YAG laser, which has a nominal energy of 30 mJ/pulse, is being used. This beam is conducted from the laser to the mass spectrometer by means of coated UV grade right angle prisms. The radiation is introduced into the vacuum system through a Ceramaseal cultured crystal quartz viewport, and exits through a sapphire window, which is angled at 15 degrees with respect to the beam axis. The pulse energies are measured with a Molectron JD 2000 Joulemeter Ratiometer positioned outside the sapphire window. The laser beam can be focused into the center of the ion source and into the molecular beam with a coated, 150 mm coated UV grade quartz lens. This lens can be removed to obtain a larger, lower density laser beam. The ion source is fitted with a diaphragm which prevents the laser beam from striking any portion of the ion source structure to avoid possible surface desorption effects. The mass spectrometer output is recorded by a Hewlett-Packard Model 5422 multichannel analyzer which is triggered from the laser pulse as in the kinetic experiments discussed above. This provides time-resolved measurements of the photolysis (and any MPI) products, which can be distinguished from the baseline reaction products generated in the flow reactor.

The laser photolysis apparatus has been completely assembled. However, the project was delayed by equipment problems and so it was not possible to carry out the initial experiments in time for inclusion in this report.

## SECTION 5

### SUMMARY

An investigation of chlorine oxides present at temperatures and pressures typical of the Antarctic stratosphere was carried out. A series of low temperature flow reactors were constructed which were suitable for use in conjunction with molecular beam mass spectrometric techniques. Six chemical systems were investigated and evaluated for their utility in the identification of ClO dimer and the characterization of its kinetic and photochemical behavior.

These studies showed that the gas phase chlorine-oxygen system at low temperatures was quite complex; characterization of these systems was required before the major tasks could be undertaken. ClO dimer was unambiguously identified and found to be thermodynamically very stable under stratospheric conditions. It was also found that any system which contained ClO<sub>2</sub> and ClO also contained a larger oxide. This oxide was also identified by mass spectrometric and velocity analysis techniques to be Cl<sub>2</sub>O<sub>3</sub>. A survey of higher oxides, which have been postulated as possible chlorine sinks in the stratosphere, was also carried out.

The rates of formation of ClO dimer were measured as a function of temperature and pressure. Measurements were made of both the decay of ClO and the formation of the dimer, and it was therefore possible to determine that essentially all of the ClO was converted to the dimer under stratospheric conditions, and not to other species. Rate constants were deduced from the rate data, and found to range from 1 to  $8 \times 10^{-13}$  cm<sup>3</sup>/molecule s at temperatures from -20 to -70°C and pressures from 30 to 117 torr.

The experimental problems in determining the reaction products produced by the photolysis of the dimer were analyzed, a suitable experiment devised, and the apparatus assembled. Preliminary data have not been obtained at the time of this report.

## SECTION 6

### CONCLUSIONS AND RECOMMENDATIONS FOR ADDITIONAL RESEARCH

The research performed on this program demonstrates the power of molecular beam mass spectrometry for the study of transient processes involving complex species. The dimer  $\text{Cl}_2\text{O}_2$  and the adduct  $\text{Cl}_2\text{O}_3$  were positively identified, and limits were placed on the concentrations of higher oxides which had been postulated as being significant in the chlorine-oxygen system under stratospheric conditions. The rate of formation of ClO dimer was determined by simultaneous measurements of the disappearance of ClO and the appearance of  $\text{Cl}_2\text{O}_2$ . These measurements show that the formation of the dimer is the principal ClO reaction under stratospheric conditions. Experiments were designed, and equipment set up, for the unambiguous determination of the photolysis of ClO dimer.

Additional research related to the role of chlorine oxides in the stratosphere depletion of ozone include:

- Determination of the photolysis products of ClO dimer.
- Determination of the rate of formation of  $\text{Cl}_2\text{O}_3$ .
- Determination of the photolysis products of  $\text{Cl}_2\text{O}_3$ .
- Additional characterization of the higher chlorine oxides.
- Refinement of the rates of formation of ClO dimer and elaboration of its thermochemistry.

These measurements could be made efficiently using molecular beam mass spectrometry and equipment and techniques developed on this program.

## SECTION 7

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